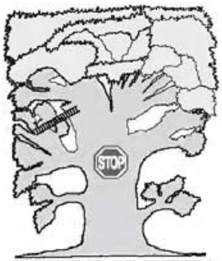

CHAPTER 6

Separation of Electronic and Nuclear Motions

> *"Any separation is a link."*
> ***Simone Weil***

Where Are We?

We are on the most important branching out of the TREE.

An Example

A colleague shows us the gas phase absorption spectra separately: of the hydrogen atom, of the chlorine atom, and of the hydrogen chloride recorded in the ultraviolet and visible (UV-VIS), infrared (IR) and microwave ranges. In the IR range, neither the hydrogen atom nor the chlorine atom have any electromagnetic wave absorption. However, on the other hand, the hydrogen chloride diatomic molecule that is formed by these two atoms has a very rich absorption spectrum with a quasi-regular and mysterious structure shown in Fig. 6.6 on p. 286. If the theory given in the previous chapters is correct, then it should explain every detail of such a strange spectrum. We also hope we will understand why such a spectrum may appear.

What Is It All About?

Ideas of Quantum Chemistry, Second Edition. http://dx.doi.org/10.1016/B978-0-444-59436-5.00006-4

Nuclei are thousands of times heavier than electrons. As an example, let us take the hydrogen atom. From the conservation of momentum law, it follows that the proton moves 1840 times slower than the electron. In a polyatomic system, while a nucleus moves a little, an electron travels many times through the molecule. It seems that much can be simplified when assuming electronic motion in a field created by immobile nuclei. This concept is behind what is called *adiabatic approximation*, in which the motions of the electrons and the nuclei are separated.[1] Only after this approximation is introduced can we obtain the fundamental concept of chemistry: the molecular structure in 3-D space.

The separation of the electronic and nuclear motions will be demonstrated in detail by taking the example of a diatomic molecule.

Why Is This Important?

The separation of the electronic and nuclear motions represents a fundamental approximation of quantum chemistry. Without this, chemists would lose their *basic model of the molecule*: the 3-D structure with the nuclei occupying some positions in 3-D space, with chemical bonds, etc. This is why this chapter occupies the *central* position on the TREE.

What Is Needed?

- Postulates of quantum mechanics (Chapter 1)
- Separation of the center-of-mass motion (see Appendix I available at booksite.elsevier.com/978-0-444-59436-5 on p. e93)
- Rigid rotator (Chapter 4)
- Harmonic and Morse oscillators (Chapter 4)
- Conclusions from group theory (see Appendix C available at booksite.elsevier.com/978-0-444-59436-5 p. e17, advised)
- Dipole moment (see Appendix X available at booksite.elsevier.com/978-0-444-59436-5 p. e169, occasionally used)

Classical Works

A fundamental approximation (called the Born-Oppenheimer approximation) was introduced in a paper called "*Zur Quantentheorie der Molekeln*" by Max Born and Julius Robert Oppenheimer in *Annalen der Physik, 84,* 457 (1927). The approximation follows from the fact that nuclei are much heavier than electrons. ★ The conical intersection problem was first recognized by three young and congenial Hungarians: Janos (later John) von Neumann and Jenő Pál (later Eugene) Wigner in the papers "*Über merkwürdige diskrete Eigenwerte*" in *Physikalische Zeitschrift, 30,* 465 (1929), and "*Über das Verhalten von Eigenwerten bei adiabatischen Prozessen*" also published in *Physikalische Zeitschrift, 30,* 467 (1929), and later in a paper "*Crossing of Potential Surfaces*" by Edward Teller published in the *Journal of Physical Chemistry 41,* 109 (1937). ★ Gerhard Herzberg was the greatest spectroscopist of the 20th century, author of the fundamental three-volume work: *Spectra of Diatomic Molecules* (1939), *Infrared and Raman Spectra of Polyatomic Molecules* (1949) and *Electronic Spectra of Polyatomic Molecules* (1966). ★ The world's first computational papers using a rigorous approach that went beyond the Born-Oppenheimer approximation for molecules were two articles by Włodzimierz Kołos and Lutosław Wolniewicz. The first was "*The coupling between electronic and nuclear motion and the relativistic effects in the ground state of the* H_2 *molecule,*" published in *Acta Physica Polonica, 20,* 129 (1961). The second was "*A complete non-relativistic treatment of the* H_2 *molecule,*" published in *Physics Letters, 2,* 222 (1962). ★ The discovery of the conical intersection and the funnel effect in photochemistry is attributed to Howard E. Zimmerman: *Molecular Orbital Correlation Diagrams, Möbius Systems, and Factors Controlling Ground- and Excited-State Reactions* [*Journal of the American Chemical Society, 88,* 1566

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[1] This does not mean that electrons and nuclei move independently. We obtain two coupled equations: one for the motion of the electrons in the field of the fixed nuclei, and the other for the motion of the nuclei in the potential averaged over the electronic positions.

(1966)] and to Josef Michl [*Journal of Molecular Photochemistry*, *4*, 243 (1972)]. Important contributions in this domain were also made by Lionel Salem and Christopher Longuet-Higgins.

John von Neumann (1903–1957), known as Jancsi (then Johnny), was the wunderkind of a top Hungarian banker. (Jancsi showed off at receptions by reciting from memory all the phone numbers after reading a page of the phone book.) He attended the famous Lutheran High School in Budapest, the same one as Jenó Pál Wigner (who later used the name Eugene). In 1926, von Neumann received his chemistry engineering diploma; and in the same year, he completed his Ph.D. in mathematics at the University of Budapest. He finally emigrated to the United States and founded the Princeton Advanced Study Institute. John von Neumann was a mathematical genius who contributed to the mathematical foundations of quantum theory, computers, and game theory.

von Neumann made a strange offer of a professorship at the Advanced Study Institute to Stefan Banach from the John Casimir University in Lwów. He handed him a check with "1" handwritten on it and asked Banach to add as many zeros as he wanted. "*This is not enough money to persuade me to leave Poland,*" answered mathematician Banach.

Edward Teller (1908–2004), American physicist of Hungarian origin and professor at the George Washington University, the University of Chicago, and the University of California. Teller left Hungary in 1926, received his Ph.D. in 1930 at the University of Leipzig, and fled Nazi Germany in 1935. Teller was the project leader of the U.S. hydrogen bomb project in Los Alamos, believing that this was the way to overthrow communism ("I am passionately opposed to killing, but I am even more passionately fond of freedom"). The hydrogen bomb patent is owned by Teller and Stanisław Ulam.

Eugene Paul Wigner (1902–1995), American chemist, physicist and mathematician of Hungarian origin and professor at Princeton University. At the age of 11, Wigner, a schoolboy from Budapest, was in a sanatorium in Austria with suspected tuberculosis. Lying for hours on a deck chair reading books, he was seduced by the beauty of mathematics (fortunately, it turned out that he did not have tuberculosis).

In 1915, Wigner entered the Lutheran High School in Budapest. Fulfilling the wishes of his father, who dreamed of having a successor in managing the familial tannery, Wigner graduated from the Technical University in Budapest as a chemist. In 1925, at the Technical University in Berlin, he defended his Ph.D. thesis on chemical kinetics "*Bildung und Zerfall von Molekülen,*" under the supervision of Michael Polanyi, a pioneer in the study of chemical reactions. In 1926 Wigner left the tannery.

By chance he was advised by his colleague von Neumann to focus on group theory (where he obtained the most spectacular successes). Wigner was the first to understand the main features of the nuclear forces. In 1963 he won the Nobel Prize "*for his contributions to the theory of the atomic nucleus and elementary particles, particularly through the discovery and application of fundamental symmetry principles.*"

Christopher Longuet-Higgins (1923–2004), professor at the University of Sussex, Great Britain, began his scientific career as a theoretical chemist. His main achievements are connected with conical intersection, as well as with the introduction of permutational groups in the theoretical explanation of the spectra of flexible molecules.

Longuet-Higgins was elected the member of the Royal Society of London for these contributions. He turned to artificial intelligence at the age of 40, and in 1967, he founded the Department of Machine Intelligence and Perception at the University of Edinburgh. Longuet-Higgins investigated machine perception of speech and music. His contribution to this field was recognized by the award of an honorary doctorate in Music by Sheffield University. *Courtesy of Professor John D.Roberts.*

6.1 Separation of the Center-of-Mass Motion

Space-Fixed Coordinate System (SFCS)

Let us consider first a diatomic molecule with the nuclei labeled a, b, and n electrons. Let us choose a Cartesian coordinate system in our laboratory (called the *space-fixed coordinate system, or SFCS*) with the origin located at an arbitrarily chosen point and with arbitrary orientation of the axes[2]. The nuclei have the following positions: $\boldsymbol{R}_a = (X_a, Y_a, Z_a)$ and $\boldsymbol{R}_b = (X_b, Y_b, Z_b)$, while electron i has the coordinates x_i', y_i', z_i'.

We write the Hamiltonian for the system (as discussed in Chapter 1):

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2M_a}\Delta_a - \frac{\hbar^2}{2M_b}\Delta_b - \sum_{i=1}^{n}\frac{\hbar^2}{2m}\Delta_i' + V, \tag{6.1}$$

where the first two terms stand for the kinetic energy operators of the nuclei, the third term corresponds to the kinetic energy of the electrons (m is the electron mass, and all Laplacians are in the SFCS), and V denotes the Coulombic potential energy operator (interaction of all the

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[2] For example, right in the center of the Norwich market square.

particles, nucleus-nucleus, nuclei-electrons, and electrons-electrons)[3]:

$$V = \frac{\mathcal{Z}_a \mathcal{Z}_b e^2}{R} - \mathcal{Z}_a \sum_i \frac{e^2}{r_{ai}} - \mathcal{Z}_b \sum_i \frac{e^2}{r_{bi}} + \sum_{i<j} \frac{e^2}{r_{ij}}. \tag{6.2}$$

While we are not interested in collisions of our molecule with a wall or similar obstruction, we may consider a separation of the motion of the center of mass, and then forget about the motion and focus on the rest (i.e., on the *relative* motion of the particles).

New Coordinates

The total mass of the molecule is $M = M_a + M_b + mn$. The components of the center-of-mass position vector are

$$X = \frac{1}{M}\left(M_a X_a + M_b X_b + \sum_i m x_i'\right)$$

$$Y = \frac{1}{M}\left(M_a Y_a + M_b Y_b + \sum_i m y_i'\right)$$

$$Z = \frac{1}{M}\left(M_a Z_a + M_b Z_b + \sum_i m z_i'\right).$$

Now, we decide to abandon this coordinate system (SFCS). Instead of the old coordinates, we will choose a new set of $3n + 6$ coordinates (see Appendix I available at booksite.elsevier.com/978-0-444-59436-5 on p. e93, choice II):

- Three center-of-mass coordinates: X, Y, Z
- Three components of the vector $\boldsymbol{R} = \boldsymbol{R}_a - \boldsymbol{R}_b$ that point to nucleus a from nucleus b
- $3n$ electronic coordinates $x_i = x_i' - \frac{1}{2}(X_a + X_b)$, and similarly, for y_i and z_i, for $i = 1, 2, \ldots n$, which show the electron's position with respect to the geometric center[4] of the molecule.

Hamiltonian in the New Coordinates

The new coordinates have to be introduced into the Hamiltonian. To this end, we need the second derivative operators in the old coordinates to be expressed by the new ones. To begin

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[3] Do not confuse coordinate Z with nuclear charge $\mathcal{Z}$.

[4] If the origin were chosen in the center of mass instead of the geometric center, V becomes mass-dependent (J. Hinze, A. Alijah and L. Wolniewicz, *Pol. J. Chem., 72,* 1293 (1998); cf. also see Appendix I available at booksite.elsevier.com/978-0-444-59436-5, example 2. We want to avoid this.

with (similarly as in Appendix I available at booksite.elsevier.com/978-0-444-59436-5), let us construct the *first* derivative operators:

$$\begin{aligned}\frac{\partial}{\partial X_a} &= \frac{\partial X}{\partial X_a}\frac{\partial}{\partial X} + \frac{\partial Y}{\partial X_a}\frac{\partial}{\partial Y} + \frac{\partial Z}{\partial X_a}\frac{\partial}{\partial Z} + \frac{\partial R_x}{\partial X_a}\frac{\partial}{\partial R_x} + \frac{\partial R_y}{\partial X_a}\frac{\partial}{\partial R_y} + \frac{\partial R_z}{\partial X_a}\frac{\partial}{\partial R_z} \\ &\quad + \sum_i \frac{\partial x_i}{\partial X_a}\frac{\partial}{\partial x_i} + \sum_i \frac{\partial y_i}{\partial X_a}\frac{\partial}{\partial y_i} + \sum_i \frac{\partial z_i}{\partial X_a}\frac{\partial}{\partial z_i} \\ &= \frac{\partial X}{\partial X_a}\frac{\partial}{\partial X} + \frac{\partial R_x}{\partial X_a}\frac{\partial}{\partial R_x} + \sum_i \frac{\partial x_i}{\partial X_a}\frac{\partial}{\partial x_i} = \frac{M_a}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial R_x} - \frac{1}{2}\sum_i \frac{\partial}{\partial x_i}\end{aligned}$$

and the same goes for the coordinates Y_a and Z_a. For the nucleus b, the expression is a little bit different: $\frac{\partial}{\partial X_b} = \frac{M_b}{M}\frac{\partial}{\partial X} - \frac{\partial}{\partial R_x} - \frac{1}{2}\sum_i \frac{\partial}{\partial x_i}$.

For the first derivative operator with respect to the coordinates of the electron i, we obtain:

$$\begin{aligned}\frac{\partial}{\partial x_i'} &= \frac{\partial X}{\partial x_i'}\frac{\partial}{\partial X} + \frac{\partial Y}{\partial x_i'}\frac{\partial}{\partial Y} + \frac{\partial Z}{\partial x_i'}\frac{\partial}{\partial Z} + \frac{\partial R_x}{\partial x_i'}\frac{\partial}{\partial R_x} + \frac{\partial R_y}{\partial x_i'}\frac{\partial}{\partial R_y} + \frac{\partial R_z}{\partial x_i'}\frac{\partial}{\partial R_z} \\ &\quad + \sum_j \frac{\partial x_j}{\partial x_i'}\frac{\partial}{\partial x_j} + \sum_j \frac{\partial y_j}{\partial x_i'}\frac{\partial}{\partial y_j} + \sum_j \frac{\partial z_j}{\partial x_i'}\frac{\partial}{\partial z_j} \\ &= \frac{\partial X}{\partial x_i'}\frac{\partial}{\partial X} + \frac{\partial x_i}{\partial x_i'}\frac{\partial}{\partial x_i} = \frac{m}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial x_i}\end{aligned}$$

and the same goes for y_i' and z_i'.

Now, let us create the second derivative operators:

$$\begin{aligned}\frac{\partial^2}{\partial X_a^2} &= \left(\frac{M_a}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial R_x} - \frac{1}{2}\sum_i \frac{\partial}{\partial x_i}\right)^2 = \left(\frac{M_a}{M}\right)^2 \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial R_x^2} + \frac{1}{4}\left(\sum_i \frac{\partial}{\partial x_i}\right)^2 \\ &\quad + 2\frac{M_a}{M}\frac{\partial}{\partial X}\frac{\partial}{\partial R_x} - \frac{\partial}{\partial R_x}\sum_i \frac{\partial}{\partial x_i} - \frac{M_a}{M}\frac{\partial}{\partial X}\sum_i \frac{\partial}{\partial x_i}, \\ \frac{\partial^2}{\partial X_b^2} &= \left(\frac{M_b}{M}\frac{\partial}{\partial X} - \frac{\partial}{\partial R_x} - \frac{1}{2}\sum_i \frac{\partial}{\partial x_i}\right)^2 = \left(\frac{M_b}{M}\right)^2 \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial R_x^2} + \frac{1}{4}\left(\sum_i \frac{\partial}{\partial x_i}\right)^2 \\ &\quad - 2\frac{M_b}{M}\frac{\partial}{\partial X}\frac{\partial}{\partial R_x} + \frac{\partial}{\partial R_x}\sum_i \frac{\partial}{\partial x_i} - \frac{M_b}{M}\frac{\partial}{\partial X}\sum_i \frac{\partial}{\partial x_i}, \\ \frac{\partial^2}{\partial \left(x_i'\right)^2} &= \left(\frac{m}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial x_i}\right)^2 = \left(\frac{m}{M}\right)^2 \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial x_i^2} + 2\frac{m}{M}\frac{\partial}{\partial X}\frac{\partial}{\partial x_i}.\end{aligned}$$

After inserting all this into the Hamiltonian [Eq. (6.1)] we obtain the Hamiltonian expressed in the new coordinates[5]:

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[5] The potential energy also has to be expressed using the new coordinates.

$$\hat{\mathcal{H}} = \left[-\frac{\hbar^2}{2M}\Delta_{XYZ}\right] + \hat{H}_0 + \hat{H}', \tag{6.3}$$

where the first term means the center-of-mass kinetic energy operator and $\hat{H}_0$ is the *electronic Hamiltonian* (*clamped nuclei Hamiltonian*):

$$\hat{H}_0 = -\sum_i \frac{\hbar^2}{2m}\Delta_i + V, \tag{6.4}$$

while $\Delta_i \equiv \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$ and

$$\hat{H}' = -\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}} + \hat{H}'', \tag{6.5}$$

with $\Delta_{\boldsymbol{R}} \equiv \frac{\partial^2}{\partial R_x^2} + \frac{\partial^2}{\partial R_y^2} + \frac{\partial^2}{\partial R_z^2}$, where

$$\hat{H}'' = \left[-\frac{\hbar^2}{8\mu}\left(\sum_i \nabla_i\right)^2 + \frac{\hbar^2}{2}\left(\frac{1}{M_a} - \frac{1}{M_b}\right)\nabla_{\boldsymbol{R}}\sum_i \nabla_i\right],$$

and μ denotes the reduced mass of the two nuclei ($\mu^{-1} = M_a^{-1} + M_b^{-1}$).

The $\hat{H}_0$ does not contain the kinetic energy operator of the nuclei, but it does contain all the other terms (this is why it is called the *electronic* or *clamped nuclei Hamiltonian*): the first term stands for the kinetic energy operator of the electrons, and V means the potential energy corresponding to the Coulombic interaction of all particles. The first term in the operator $\hat{H}'$ (i.e., $-\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}}$), denotes the kinetic energy operator of the nuclei[6], while the operator $\hat{H}''$ couples the motions of the nuclei and electrons[7].

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[6] What moves is a particle of reduced mass μ and coordinates R_x, R_y, and R_z. This means that the particle has the position of nucleus a, whereas nucleus b is at the origin. Therefore, this term accounts for the vibrations of the molecule (changes in length of $\boldsymbol{R}$), as well as its rotations (changes in orientation of $\boldsymbol{R}$).

[7] The first of these two terms contains the reduced mass of the two nuclei, where ∇_i denotes the nabla operator for electron i, $\nabla_i \equiv \boldsymbol{i}\frac{\partial}{\partial x_i} + \boldsymbol{j}\frac{\partial}{\partial y_i} + \boldsymbol{k}\frac{\partial}{\partial z_i}$ with $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ the unit vectors along the x-,y-, and z-axes. The second term is nonzero only for the heteronuclear case and contains the mixed product of nablas: $\nabla_R \nabla_i$ with $\nabla_{\boldsymbol{R}} = \boldsymbol{i}\frac{\partial}{\partial R_x} + \boldsymbol{j}\frac{\partial}{\partial R_y} + \boldsymbol{k}\frac{\partial}{\partial R_z}$ and R_x, R_y, R_z as the components of the vector $\boldsymbol{R}$.

After Separation of the Center-of-Mass Motion

After separation of the center-of-mass motion [the first term in Eq. (6.3) is gone; see Appendix I available at booksite.elsevier.com/978-0-444-59436-5 on p. e93], we obtain the eigenvalue problem of the Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}'. \tag{6.6}$$

This is an exact result, fully equivalent to the Schrödinger equation.

6.2 Exact (Non-Adiabatic) Theory

The total wave function that describes both electrons and nuclei can be proposed in the following form[8] ($\mathcal{N} = \infty$):

$$\boxed{\Psi(\boldsymbol{r}, \boldsymbol{R}) = \sum_k^{\mathcal{N}} \psi_k(\boldsymbol{r}; R) f_k(\boldsymbol{R}),} \tag{6.7}$$

where $\psi_k(\boldsymbol{r}; R)$ are the eigenfunctions of $\hat{H}_0$:

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[8] Where would such a form of the wave function come from?

If the problem were solved exactly, then the solution of the Schrödinger equation could be sought; e.g., by using the Ritz method (p. 238). Then we have to decide what kind of basis set to use. We could use two auxiliary complete basis sets: one that depended on the electronic coordinates $\{\bar{\psi}_k(\boldsymbol{r})\}$, and another that depended on the nuclear coordinates $\{\bar{\phi}_l(\boldsymbol{R})\}$. The complete basis set for the Hilbert space of our system could be constructed as a Cartesian product $\{\bar{\psi}_k(\boldsymbol{r})\} \times \{\bar{\phi}_l(\boldsymbol{R})\}$; i.e., all possible product-like functions $\bar{\psi}_k(\boldsymbol{r})\bar{\phi}_l(\boldsymbol{R})$. Thus, the wave function could be expanded in a series, as follows:

$$\begin{aligned}\Psi(\boldsymbol{r}, \boldsymbol{R}) &= \sum_{kl} c_{kl}\bar{\psi}_k(\boldsymbol{r})\bar{\phi}_l(\boldsymbol{R}) = \sum_k^{\mathcal{N}} \bar{\psi}_k(\boldsymbol{r}) \left[\sum_l c_{kl}\bar{\phi}_l(\boldsymbol{R})\right] \\ &= \sum_k^{\mathcal{N}} \bar{\psi}_k(\boldsymbol{r}) f_k(\boldsymbol{R}),\end{aligned}$$

where $f_k(\boldsymbol{R}) = \sum_l c_{kl}\bar{\phi}_l(\boldsymbol{R})$ stands for a to-be-sought coefficient depending on $\boldsymbol{R}$ (rovibrational function). If we were dealing with complete sets, then both $\bar{\psi}_k$ and f_k should not depend on anything else, since a sufficiently long expansion of the terms $\bar{\psi}_k(\boldsymbol{r})\bar{\phi}_l(\boldsymbol{R})$ would be suitable to describe all possible distributions of the electrons and the nuclei.

However, we are unable to manage the complete sets. Instead, we are able to take only a few terms in this expansion. We would like them to describe the molecule reasonably well, and at the same time to have only one such term. If so, it would be reasonable to introduce a parametric dependence of the function $\bar{\psi}_k(\boldsymbol{r})$ on the position of the nuclei, which in our case of a diatomic molecule means the internuclear distance. This is equivalent to telling someone how the electrons behave when the internuclear distances have some specific values, and how they behave when the distances change.

$$\hat{H}_0(R)\psi_k(\boldsymbol{r};R)=E_k^0(R)\psi_k(\boldsymbol{r};R) \tag{6.8}$$

and depend parametrically[9] on the internuclear distance R, and $f_k(\boldsymbol{R})$ are yet unknown rovibrational functions (describing the rotations and vibrations of the molecule).

Averaging Over Electronic Coordinates

First, let us write down the Schrödinger equation with the Hamiltonian [Eq. (6.6)] and the wave function, as in Eq. (6.7):

$$(\hat{H}_0+\hat{H}')\sum_l^{\mathcal{N}}\psi_l\left(\boldsymbol{r};R\right)f_l(\boldsymbol{R})=E\sum_l^{\mathcal{N}}\psi_l\left(\boldsymbol{r};R\right)f_l(\boldsymbol{R}). \tag{6.9}$$

Let us multiply both sides by $\psi_k^*(\boldsymbol{r};R)$ and then integrate over the *electronic* coordinates $\boldsymbol{r}$ (which will be stressed by the subscript "e"):

$$\sum_l^{\mathcal{N}}\left\langle\psi_k|(\hat{H}_0+\hat{H}')[\psi_l f_l]\right\rangle_e=E\sum_l^{\mathcal{N}}\langle\psi_k|\psi_l\rangle_e f_l. \tag{6.10}$$

On the right side of Eq. (6.10), we profit from the orthonormalization condition $\langle\psi_k|\psi_l\rangle_e=\delta_{kl}$, and on the left side, we recall that ψ_k is an eigenfunction of $\hat{H}_0$:

$$E_k^0 f_k+\sum_l^{\mathcal{N}}\left\langle\psi_k|\hat{H}'[\psi_l f_l]\right\rangle_e=Ef_k. \tag{6.11}$$

Now, let us focus on the expression $\hat{H}'(\psi_l f_l)=-\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}}(\psi_l f_l)+\hat{H}''(\psi_l f_l)$, which we have in the integrand in Eq. (6.11). Let us concentrate on the first of these terms:

$$\begin{aligned}-\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}}(\psi_l f_l)&=-\frac{\hbar^2}{2\mu}\nabla_{\boldsymbol{R}}\nabla_{\boldsymbol{R}}(\psi_l f_l)=-\frac{\hbar^2}{2\mu}\nabla_{\boldsymbol{R}}[\psi_l\nabla_{\boldsymbol{R}}f_l+(\nabla_{\boldsymbol{R}}\psi_l)f_l]\\&=-\frac{\hbar^2}{2\mu}[\nabla_{\boldsymbol{R}}\psi_l\nabla_{\boldsymbol{R}}f_l+\psi_l\Delta_{\boldsymbol{R}}f_l+(\Delta_{\boldsymbol{R}}\psi_l)f_l+\nabla_{\boldsymbol{R}}\psi_l\nabla_{\boldsymbol{R}}f_l]\\&=-\frac{\hbar^2}{2\mu}[2\left(\nabla_{\boldsymbol{R}}\psi_l\right)\left(\nabla_{\boldsymbol{R}}f_l\right)+\psi_l\Delta_{\boldsymbol{R}}f_l+(\Delta_{\boldsymbol{R}}\psi_l)f_l].\end{aligned} \tag{6.12}$$

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[9] For each value of R, we have a different formula for ψ_k.

After inserting the result into $\left\langle \psi_k | \hat{H}'(\psi_l f_l) \right\rangle_e$ and recalling Eq. (6.5), we have

$$\begin{aligned}\left\langle \psi_k | \hat{H}'[\psi_l f_l] \right\rangle_e &= 2\left(-\frac{\hbar^2}{2\mu}\right) \langle \psi_k | \nabla_{\boldsymbol{R}} \psi_l \rangle_e \nabla_{\boldsymbol{R}} f_l + \langle \psi_k | \psi_l \rangle_e \left(-\frac{\hbar^2}{2\mu}\right) \Delta_{\boldsymbol{R}} f_l \\ &\quad + \left\langle \psi_k \left| \left(-\frac{\hbar^2}{2\mu}\right) \Delta_{\boldsymbol{R}} \psi_l \right.\right\rangle_e f_l + \left\langle \psi_k | \hat{H}'' \psi_l \right\rangle_e f_l \\ &= (1-\delta_{kl})\left(-\frac{\hbar^2}{\mu}\right) \langle \psi_k | \nabla_{\boldsymbol{R}} \psi_l \rangle_e \nabla_{\boldsymbol{R}} f_l - \delta_{kl} \frac{\hbar^2}{2\mu} \Delta_{\boldsymbol{R}} f_l + H'_{kl} f_l, \quad (6.13)\end{aligned}$$

with

$$H'_{kl} \equiv \left\langle \psi_k | \hat{H}' \psi_l \right\rangle_e .$$

At that point, we obtain the following form of Eq. (6.11):

$$E_k^0 f_k + \sum_l^{\mathcal{N}} \left[(1-\delta_{kl})\left(-\frac{\hbar^2}{\mu}\right) \langle \psi_k | \nabla_{\boldsymbol{R}} \psi_l \rangle_e \nabla_{\boldsymbol{R}} f_l - \delta_{kl} \frac{\hbar^2}{2\mu} \Delta_{\boldsymbol{R}} f_l + H'_{kl} f_l \right] = E f_k .$$

Here, we have profited from the equality $\langle \psi_l | \nabla_{\boldsymbol{R}} \psi_l \rangle_e = 0$, which follows from the differentiation of the normalization condition[10] for the function ψ_l.

Non-Adiabatic Nuclear Motion

Grouping all the terms with f_l on the left side, we obtain a set of $\mathcal{N}$ equations:

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\boldsymbol{R}} + E_k^0(R) + H'_{kk}(R) - E \right] f_k = -\sum_{l(\neq k)}^{\mathcal{N}} \Theta_{kl} \, f_l, \qquad (6.14)$$

for $k = 1, 2, \ldots \mathcal{N}$ with the non-adiabatic coupling operators

$$\Theta_{kl} = -\frac{\hbar^2}{\mu} \langle \psi_k | \nabla_{\boldsymbol{R}} \psi_l \rangle_e \nabla_{\boldsymbol{R}} + H'_{kl}. \qquad (6.15)$$

Note that the operator H'_{kl} depends on the length of the vector $\boldsymbol{R}$, but not on its direction.[11]

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[10] We assume that the phase of the wave function $\psi_k(\boldsymbol{r}; R)$ does not depend on R; i.e., $\psi_k(\boldsymbol{r}; R) = \bar{\psi}_k(\boldsymbol{r}; R) \exp(i\phi)$, where $\bar{\psi}_k$ is a real function and $\phi \neq \phi(R)$. This immediately gives $\langle \psi_k | \nabla_{\boldsymbol{R}} \psi_k \rangle_e = \langle \bar{\psi}_k | \nabla_{\boldsymbol{R}} \bar{\psi}_k \rangle_e$, which is ~~zero~~, always from differentiating the normalization condition. Indeed, the normalization condition: $\int \psi_k^2 \mathrm{d}\tau_e = 1$. Hence, $\nabla_{\boldsymbol{R}} \int \psi_k^2 \mathrm{d}\tau_e = 0$, or $2 \int \psi_k \nabla_{\boldsymbol{R}} \psi_k \mathrm{d}\tau_e = 0$. Without this ~~approximation, we will surely have trouble.~~ Is this valid?

[11] This follows from the fact that we have in $\hat{H}'$ [see Eq. (6.5)] the products of nablas (i.e., scalar products). The scalar products do not change upon rotation because both vectors involved rotate in the same way and the angle between them does not change.

Equation (6.14) is equivalent to the Schrödinger equation.

Equations (6.14) and (6.15) have been derived under the assumption that ψ_k of Eq. (6.7) satisfies Eq. (6.8). If instead of $\psi_k(\boldsymbol{r};R)$, we use a (generally non-orthogonal) complete set $\left\{\bar{\psi}_k(\boldsymbol{r};R)\right\}$ in Eq. (6.7), Eqs. (6.14) and (6.15) would change to

$$\left[-\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}} + \bar{E}_k(R) + H'_{kk}(R) - E\right] f_k = -\sum_{l(\neq k)}^{\mathcal{N}} \Theta_{kl}\, f_l, \tag{6.16}$$

for $k = 1, 2, \ldots \mathcal{N}$ with the non-adiabatic coupling operators

$$\Theta_{kl} = -\frac{\hbar^2}{\mu}\langle\bar{\psi}_k|\nabla_{\boldsymbol{R}}\bar{\psi}_l\rangle_e \nabla_{\boldsymbol{R}} + H'_{kl} + \langle\bar{\psi}_k|\bar{\psi}_l\rangle_e\left(-\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}}\right) \tag{6.17}$$

and $\bar{E}_k(R) \equiv \left\langle\bar{\psi}_k|\hat{H}_0\bar{\psi}_k\right\rangle_e$. Functions $\bar{\psi}_k(\boldsymbol{r};R)$ may be chosen as the wave functions with some chemical significance.

6.3 Adiabatic Approximation

If the curves $E_k^0(R)$ for different k are well separated in the energy scale, we may expect that the coupling between them is small, and therefore all Θ_{lk} for $k \neq l$ may be set equal to zero. This is called the *adiabatic approximation*. In this approximation, we obtain from Eq. (6.14):

$$\left[-\frac{\hbar^2}{2\mu}\Delta_{\boldsymbol{R}} + E_k^0(R) + H'_{kk}(R)\right] f_k(\boldsymbol{R}) = E f_k(\boldsymbol{R}), \tag{6.18}$$

where the diagonal correction $H'_{kk}(R)$ is usually very small compared to $E_k^0(R)$.

In the adiabatic approximation, the wave function is approximated by a product

$$\Psi \approx \psi_k(\boldsymbol{r};R) f_k(\boldsymbol{R}) \tag{6.19}$$

The function $f_k(\boldsymbol{R})$ depends explicitly not only on R, but also on the direction of vector $\boldsymbol{R}$, and therefore it will describe future vibrations of the molecule (changes of R), as well as its rotations (changes of the direction of $\boldsymbol{R}$).

A Simple Analogy

Let us pause a moment to get a sense of the adiabatic approximation.

To some extent, the situation resembles an attempt to describe a tourist (an electron) and the Alps (nuclei). Not only the tourist moves, but also the Alps, as has been quite convincingly proved by geologists.[12] The probability of encountering the tourist may be described by a "*wave function*" computed for a fixed position of the mountains (shown by a map bought in a shop). This is a very good approximation because when the tourist wanders over hundreds of miles, the beloved Alps move a tiny distance, so the map seems to be perfect all the time. On the other hand, the probability of having the Alps in a given configuration is described by the geologists' "wave function" f, saying e.g. what is the probability that the distance between the Matterhorn and the Jungfrau is equal to R. When the tourist revisits the Alps after a period of time (say, a few million years), the mountains will have changed (the new map bought in the shop will reflect this fact). The probability of finding the tourist may again be computed from the new wave function, which is valid for the new configuration of the mountains (a parametric dependence). Therefore, the probability of finding the tourist in the spot indicated by the vector $\boldsymbol{r}$ at a given configuration of the mountains $\boldsymbol{R}$ can be approximated by a product[13] of the probability of finding the mountains at this configuration $|f_k(\boldsymbol{R})|^2 d\boldsymbol{R}$ and the probability $|\psi_k(\boldsymbol{r};\boldsymbol{R})|^2 d\boldsymbol{r}$ of finding the tourist in the position shown by the vector $\boldsymbol{r}$, when the mountains have this particular configuration $\boldsymbol{R}$. In the case of our molecule, this means the adiabatic approximation (a product-like form), Eq. (6.19).

This parallel fails in one important way: the Alps do not move in the potential created by tourists, the dominant geological processes are tourist-independent. Contrary to this, as we will soon see, nuclear motion is dictated by the electrons through the potential averaged over the electronic motion.

6.4 Born-Oppenheimer Approximation

In the adiabatic approximation, $H'_{kk} = \int \psi_k^* H' \psi_k \mathrm{d}\tau_e$ represents a small correction to $E_k^0(R)$. Neglecting this correction results in the Born-Oppenheimer approximation:

$$H'_{kk} = 0.$$

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[12] The continental plates collide like billiard balls in a kind of quasi-periodic oscillation. During the current oscillation, the India plate, which moved at a record speed of about 20 cm a year, hit the Euroasiatic plate. This is why the Himalayan mountains are so beautiful. The collision continues, and the Himalayas will be even more beautiful someday. Europe was hit from the south by a few plates moving at only about 4 cm a year, and this is why Alps are lower than Himalayas. While visiting the Atlantic coast of Maine, I wondered that the color of the rocks was very similar to those I remembered from Brittany, in France. That was it! Once upon a time, the two coasts made a common continent. Later, we had to rediscover America. The Wegener theory of continental plate tectonics, when created in 1911, was viewed as absurd, although the mountain *ranges* suggested that some plates were colliding.

[13] This is an approximation because in the non-adiabatic (i.e., fully correct) approach, the total wave function is a superposition of many such products, corresponding to various electronic and rovibrational wave functions.

Note that in the Born-Oppenheimer approximation, the potential energy for the motion of the nuclei $E_k^0(R)$ is independent of the mass of the nuclei, whereas in the adiabatic approximation, the potential energy $E_k^0(R) + H'_{kk}(R)$ depends on the mass.

Julius Robert Oppenheimer (1904–1967), American physicist and professor at the University of California in Berkeley, the California Institute of Technology in Pasadena, and the Institute for Advanced Study in Princeton. From 1943 to 1945, Oppenheimer headed the Manhattan Project (atomic bomb).

From John Slater's autobiography:

"Robert Oppenheimer was a very brilliant physics undergraduate at Harvard during the 1920s, the period when I was there on the faculty, and we all recognized that he was a person of very unusual attainments. Rather than going on for his graduate work at Harvard, he went to Germany, and worked with Born, developing what has been known as the Born-Oppenheimer approximation."

. . . And a Certain Superiority of Theory Over Experiment

In experiments, every chemist finds his molecule confined close to a minimum of the electronic energy hypersurface (most often of the ground state). A powerful theory might be able to predict the results of experiments even for the nuclear configurations that are far from those that are accessible for current experiments. This is the case with quantum mechanics, which is able to describe in detail what would happen to the electronic structure[14], if the nuclear configuration were very strange; e.g., the internuclear distances were close to zero, if not exactly zero. Within the Born-Oppenheimer approximation, the theoretician is free to put the nuclei wherever he wishes. This means that we are able to discuss and then just to test "*what would be if*," even if this "*if*" were crazy. For example, some small internuclear distances are achievable at extremely large pressures. At such pressures, some additional difficult experiments have to be performed to tell us about the structure and processes. A theoretician just sets the small distances and makes a computer run. This is really exceptional: we may set some conditions that are out of reach of experiments (even very expensive ones), and we are able to tell with confidence and at low cost what will be.

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[14] We just do not have any reason to doubt it.

6.5 Vibrations of a Rotating Molecule

Our next step will be an attempt to separate rotations and oscillations within the adiabatic approximation. To this end, the function $f_k(\boldsymbol{R}) = f_k(R, \theta, \phi)$ will be proposed as a *product* of a function Y which will account for rotations (depending on θ, ϕ), and a certain function $\frac{\chi_k(R)}{R}$ describing the oscillations i.e., dependent on R

$$f_k(\boldsymbol{R}) = Y(\theta, \phi)\frac{\chi_k(R)}{R}. \tag{6.20}$$

No additional approximation is introduced in this way. We say only that the isolated molecule vibrates independently of whether it is oriented toward the Capricorn or Taurus constellations ("space is isotropic").[15] The function $\chi_k(R)$ is yet unknown, and we are going to search for it; therefore, dividing by R in (6.20) is meaningless.[16]

Now, we will try to separate the variables θ, ϕ from the variable R in Eq. (6.18); i.e., to obtain two separate equations for them. First, let us define the quantity

$$U_k(R) = E_k^0(R) + H'_{kk}(R). \tag{6.21}$$

After inserting the Laplacian (in spherical coordinates; see Appendix H available at booksite.elsevier.com/978-0-444-59436-5 on p. e91) and the product [Eq. (6.20)] into Eq. (6.18), we obtain the following series of transformations:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + U_k(R)\right]Y\frac{\chi_k}{R} = EY\frac{\chi_k}{R},$$

$$-\frac{\hbar^2}{2\mu}\left(\frac{Y}{R}\frac{\partial^2\chi_k}{\partial R^2} + \frac{\chi_k}{R}\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{\chi_k}{R}\frac{1}{R^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right) + YU_k(R)\frac{\chi_k}{R} = EY\frac{\chi_k}{R},$$

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{\chi_k}\frac{\partial^2\chi_k}{\partial R^2} + \frac{1}{Y}\left(\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{R^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)\right) + U_k(R) = E,$$

$$-\left(\frac{R^2}{\chi_k}\frac{\partial^2\chi_k}{\partial R^2}\right) + \frac{2\mu}{\hbar^2}U_k(R)R^2 - \frac{2\mu}{\hbar^2}ER^2 = \frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right).$$

The result is fascinating. The left side depends on R only, and the right side only on θ and ϕ. Both sides equal each other independently of the values of the variables. This can only happen if each side is equal to a constant (λ), the same for each. Therefore, we have

$$-\left(\frac{R^2}{\chi_k}\frac{\partial^2\chi_k}{\partial R^2}\right) + \frac{2\mu}{\hbar^2}U_k(R)R^2 - \frac{2\mu}{\hbar^2}ER^2 = \lambda \tag{6.22}$$

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[15] It is an assumption about "the space", which is assumed not to be changed by the presence of the Capricorn, Taurus, or other constellation.

[16] In the case of polyatomics, the function $f_k(\boldsymbol{R})$ may be more complicated because some vibrations (e.g., a rotation of the CH_3 group) may contribute to the total angular momentum, which has to be conserved (this is related to space isotropy; cf., p. 69).

$$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)=\lambda. \tag{6.23}$$

Now, we are amazed to see that Eq. (6.23) is identical (cf., p. 199) to that which appeared as a result of the transformation of the Schrödinger equation for a rigid rotator, Y denoting the corresponding wave function. As we know from p. 200, this equation has a solution only if $\lambda = -J(J+1)$, where $J = 0, 1, 2, \ldots$ Since Y stands for the rigid rotator wave function, we now concentrate exclusively on the function χ_k, which describes vibrations (changes in the length of $\boldsymbol{R}$).

After inserting the permitted values of λ into Eq. (6.22), we get

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\chi_k}{\partial R^2}\right)+U_k(R)\chi_k-E\chi_k=-\frac{\hbar^2}{2\mu R^2}J(J+1)\chi_k.$$

Let us write this equation in the form of the eigenvalue problem for the unidimensional motion of a particle (we change the partial into the regular derivative) of mass μ:

$$\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2}+V_{kJ}\right)\chi_{kvJ}(R)=E_{kvJ}\chi_{kvJ}(R) \tag{6.24}$$

with potential energy (let us stress that $R > 0$)

$$V_{kJ}(R)=U_k(R)+J(J+1)\frac{\hbar^2}{2\mu R^2}, \tag{6.25}$$

which takes the effect of centrifugal force on the vibrational motion into account. The solution χ_k, as well as the total energy E_k, have been labeled by two additional indices: the rotational quantum number J (because the potential depends on it) and the numbering of the solutions $v = 0, 1, 2, \ldots$

The solutions of Eq. (6.24) describe the vibrations of the nuclei. The function $V_{kJ} = E_k^0(R) + H'_{kk}(R) + J(J+1)\hbar^2/(2\mu R^2)$ plays the role of the potential energy curve for the motion of the nuclei.

The above equation, and therefore also

the very notion of the potential energy curve for the motion of the nuclei, appears only after the adiabatic (the product-like wave function, and H'_{kk} preserved) or the Born-Oppenheimer (the product-like wave function, but H'_{kk} removed) approximation is applied. Only in the Born-Oppenheimer approximation is the potential energy $U_k(R)$ mass-independent; e.g., the same for isotopomers H_2, HD, and D_2.

If $V_{kJ}(R)$ were a parabola (as it is for the harmonic oscillator), the system would never acquire the energy corresponding to the bottom of the parabola because the harmonic oscillator energy levels (cf., p. 190) correspond to *higher* energy. The same pertains to V_{kJ} of a more complex shape.

6.5.1 One More Analogy

The fact that the electronic energy $E_k^0(R)$ plays the role of the potential energy for vibrations not only represents the result of rather complex derivations, but is also natural and understandable. The nuclei keep together thanks to the electronic "*glue*" (we will come back to this in Chapter 8). Let us imagine two metallic balls (nuclei) in a block of transparent gum (electronic cloud), as shown in Fig. 6.1.

If we were interested in the motion of the *balls*, we would have to take the potential energy as well as the kinetic energy into account. The potential energy would depend on the distance R between the balls, in the same way as the gum's elastic energy depends on the stretching or squeezing the gum to produce a distance between the balls equal to R. Thus, the potential energy for the motion of the balls (nuclei) has to be the potential energy of the gum (electronic energy).[17]

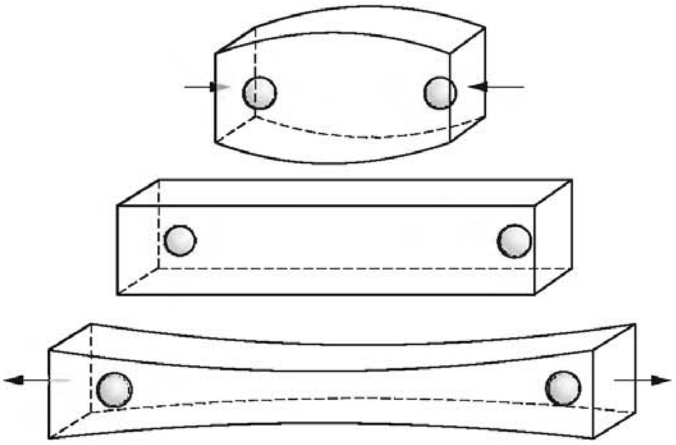

Fig. 6.1. Two metallic balls in a block of gum. How will they vibrate? This will be dictated by the elastic properties of the gum.

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[17] The adiabatic approximation is of more general importance than the separation of the electronic and nuclear motions. Its essence pertains to the problem of two coexisting time scales in some phenomena: fast and slow scales. The examples below indicate that we have to do with an important and general philosophical approach:

- In Chapter 14 on chemical reactions, we will consider slow motion along a single coordinate, and fast motions along other coordinates (in the configurational space of the nuclei). "*Vibrationally adiabatic*" approximation will also be introduced, and the slow motion will proceed in the potential energy averaged over fast motions and calculated at each fixed value of the slow coordinate.
- Similar reasoning was behind vibrational analysis in systems with hydrogen bonds [Y. Marechal and A. Witkowski, *Theor. Chim. Acta*, *9*, 116 (1967).] The authors selected a slow intermolecular motion proceeding in the potential energy averaged over fast intramolecular motions.

This situation corresponds to a non-rotating system. If we admit rotation, we would have to take the effect of centrifugal force on the potential energy (or elastic properties) of the gum into account. This effect is analogous to the second term in Eq. (6.25) for $V_{kJ}(R)$.

6.5.2 What Vibrates, What Rotates?

One may say that, as a result of averaging over electron coordinates, the electrons disappeared from the theory. The only effect of their presence are numbers: the potential energy term $U_k(R)$ of Eq. (6.21). Equation (6.24) says that the vibrating and rotating objects are bare nuclei, which seems strange because they certainly move somehow with electrons. Our intuition says that what should vibrate and rotate are atoms, not nuclei. In our example with the gum, it is evident that the iron balls should be a bit heavier since they pull the gum with them.

Where is this effect hidden? It has to be a part of the non-adiabatic effect, and can be taken into account within the non-adiabatic procedure described on p. 265. It looks quite strange. Such an obvious effect[18] is hidden in a theory that is hardly used in computational practice, because of its complexity?

If the excited electronic states are well separated from the ground electronic state $k = 0$, it turned out that one may catch a good part of this effect for the ground state by using the perturbation theory (see Chapter 5). It is possible to construct[19] a set of more and more advanced approximations for calculating the rovibrational levels. All of them stem from the following equation for the vibrational motion of the nuclei, a generalization of Eq. (6.24):

$$\left[-\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\frac{R^2}{2\mu_{\|}(R)}\frac{\mathrm{d}}{\mathrm{d}R}+W_{0J}(R)\right]\chi_{0vJ}(R)=E_{0vJ}\chi_{0vJ}(R), \tag{6.26}$$

where the operator on the left side corresponds to the kinetic energy of vibration given in Eq. (6.24), but this time, instead of the constant reduced mass μ of the nuclei, we have the mass denoted as $\mu_{\|}(R)$ that is R-dependent. The potential energy

$$W_{0J}(R)=E_0^0(R)+H'_{00}(R)+\frac{J(J+1)}{2\mu_{\perp}R^2}+\delta\mathcal{E}_{na}(R) \tag{6.27}$$

also resembles the potential energy of Eq. (6.25), but the reduced mass of the nuclei μ in the centrifugal energy, Eq. (6.25), is replaced now by a function of R denoted by $\mu_{\perp}(R)$. Visibly the nuclei are "*dressed*" by electrons, and this dressing not only is R-dependent, which is understandable, but also depends on what the nuclei are doing (vibration[20] or rotation). There is also a non-adiabatic increment $\delta\mathcal{E}_{na}(R)$, which effectively takes into account the presence

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[18] The effect is certainly small, because the mass of the electrons that make a difference (move with the nucleus) are about 1836 times smaller than the mass of the nucleus alone.

[19] K. Pachucki and J. Komasa, *J. Chem. Phys.*, *129*, 34102 (2008).

[20] The R-dependent μ was introduced by R.M. Herman and A. Asgharian, *J. Chem. Phys.*, *45*, 2433 (1966).

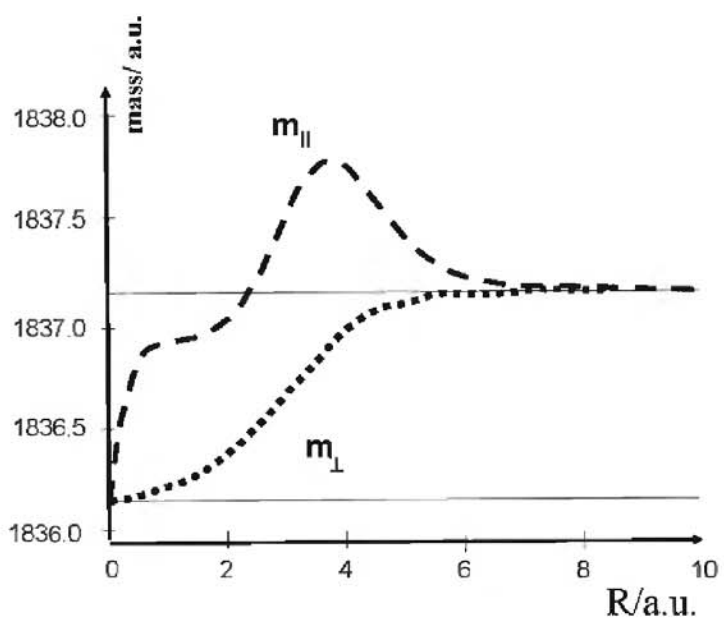

Fig. 6.2. What vibrates and what rotates in the hydrogen molecule? The variable reduced masses $\mu_{||}$ and $\mu_{\perp}$ correspond to the masses of the objects in the hydrogen molecule that vibrate ($m_{||}$) and rotate ($m_{\perp}$). Conclusion: at large distances move atoms, at very short move the bare nuclei.

of higher states. We do not give here the formulas for $\delta\mathcal{E}_{na}(R)$, $\mu_{\|}$ and $\mu_{\perp}$ (they all have been derived by Pachucki and Komasa[21]).

The following sequence of approximations can be designed:

- The Born-Oppenheimer approximation: $\mu_{||} = \mu_{\perp} = \mu$; $W_{0J}(R) = E_0^0(R) + \frac{J(J+1)}{2\mu R^2}$
- The adiabatic approximation: $\mu_{||} = \mu_{\perp} = \mu$; $W_{0J}(R) = E_0^0(R) + H'_{00}(R) + \frac{J(J+1)}{2\mu R^2}$
- The effective non-adiabatic approximation: $\mu_{||}, \mu_{\perp}$ taken as R-dependent; $W_{0J}(R) = E_0^0(R) + H'_{00}(R) + \frac{J(J+1)}{2\mu_{\perp} R^2} + \delta\mathcal{E}_{na}(R)$.

It is interesting to see what kind of object vibrates and rotates in the hydrogen molecule. As one can see from Fig. 6.2, $\mu_{||}(R = \infty) = \mu_{\perp}(R = \infty) = M_p + m$, while $\mu_{\|}(R = 0) = \mu_{\perp}(R = 0) = M_p$, where M_p stands for the mass of proton and m is the electron mass. Thus, for large R, the hydrogen *atoms* vibrate and rotate, while for very small R - only bare *protons* do. For finite nonzero values of R, the rotation-related effective atomic mass $m_{\perp}(R)$ changes monotonically, while the vibration-related effective atomic mass $m_{||}(R)$ undergoes peculiar changes exhibiting a maximum mass at about 4 a.u. (a bit larger than $M_p + m$) and additionally, an impressive plateau of about $M_p + \frac{3}{4}m$ just before going to $m_{||} = M_p$ at $R = 0$. This is what equations give; however, we have problems with rationalizing such things.

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[21] Equation (6.27) may be treated as the most general definition of the potential energy curve for the motion of the nuclei.

The approach reported is able to produce the non-adiabatic corrections to all rovibrational levels corresponding to the ground electronic state.[22]

6.5.3 The Fundamental Character of the Adiabatic Approximation—PES

In the case of a polyatomic molecule with N atoms ($N > 2$), V_{kJ} depends on $3N - 6$ variables determining the configuration of the nuclei. The function $V_{kJ}(\boldsymbol{R})$ therefore represents a surface in $(3N - 5)$-dimensional space (a *hypersurface*). This potential energy (hyper)surface $V_{kJ}(\boldsymbol{R})$, or PES, for the motion of the nuclei represents one of the most important ideas in chemistry.

This concept makes possible contact with what chemists call the spatial "*structure*" of the molecule, identified with its nuclear configuration corresponding to the minimum of the PES for the electronic ground state. It is only because of the adiabatic approximation, that we may imagine the 3-D shape of a molecule as a configuration of its nuclei bound by an electronic cloud (see Fig. 6.3). This object moves and rotates in space, and in addition, the nuclei vibrate about their equilibrium positions with respect to other nuclei (which may be visualized as a rotation-like motion close to the minimum of an energy valley).

Without the adiabatic approximation, questions about the molecular 3-D structure of the benzene molecule could only be answered in a very enigmatic way. For example:

- The molecule does not have any particular 3-D shape.
- The motion of the electrons and nuclei is very complicated.
- Correlations of motion of all the particles exist (electron-electron, nucleus-nucleus, electron-nucleus).
- These correlations are in general very difficult to elucidate.

Identical answers would be given if we were to ask about the structure of the DNA molecule. Obviously, something is going wrong, and perhaps we should expect more help from theory.

For the benzene molecule, we could answer questions like: What is the mean value of the carbon-carbon, carbon-proton, proton-proton, electron-electron, electron-proton, and electron-carbon distances in the benzene molecule in its ground and excited states? Note that because all identical particles are indistinguishable, the carbon-proton distance pertains to any carbon and any proton, and so on. To discover that the benzene molecule is essentially a planar hexagonal object would be very difficult. What could we say about a protein? A pile of paper with such numbers would give us *the* true (though non-relativistic) picture of the benzene molecule, but it would be useless, just as a map of the world with 1:1 scale would be useless for a tourist. It is just too exact. If we relied on this, progress in the investigation of the molecular world

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[22] It is worth noting that for H_2 and its lowest rovibrational level (to cite one example), making μ R-dependent [i.e., using $\mu_{||}$ and $\mu_{\perp}$ and neglecting $\delta\mathcal{E}_{na}(R)$] gives 84% of the total non-adiabatic effect, while neglecting this R-dependence [i.e., putting $\mu_{||} = \mu_{\perp} = \mu$ and taking $\delta\mathcal{E}_{na}(R)$ into account gives 15%. These two effects seem to be quite independent.

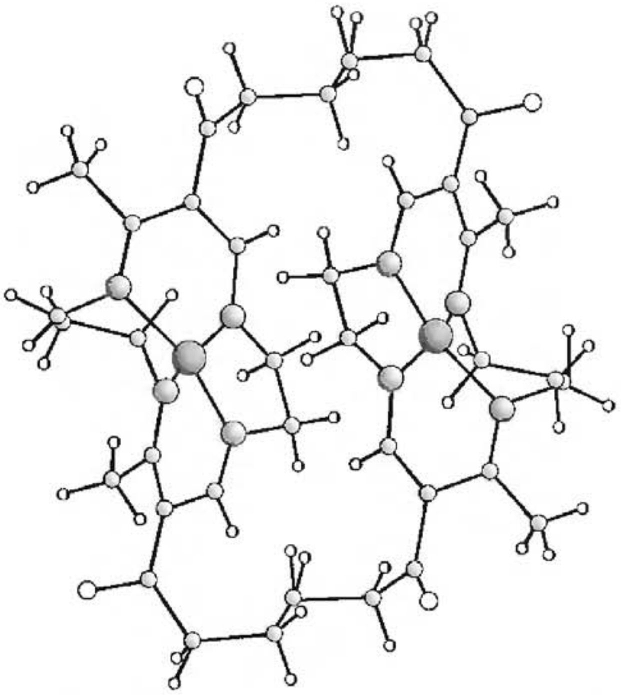

Fig. 6.3. A 3-D *model* (called the "*structure*") of a molecule allows us to focus attention on spatial and temporal relations that are similar to those we know from the macroscopic world. Although the concept of "*spatial structure*" may occasionally fail, in virtually all cases in chemistry and physics, we use a 3-D molecular model that resembles what is shown here for a particular molecule (using a 2-D projection of the 3-D model). There are "balls" and "connecting sticks." The balls represent atoms (of various sizes, and the size characterizes the corresponding element), the sticks of different length are supposed to represent what are called "chemical bonds." What should be taken seriously, and what shouldn't be? First, the scale. The real molecule is about 100000000 times smaller than the picture here. Second, the motion. This static model shows a kind of averaging over all the snapshots of the real vibrating atoms. In Chapters 8 and 11, we will see that indeed the atoms of which the molecule is composed keep together because of a pattern of interatomic chemical bonds (which characterizes the electronic state of the molecule) that to some extent resemble sticks. An atom in a molecule is never spherically symmetric (cf., Chapter 11), but can be approximated by its spherical core ("ball"). The particular molecule shown here has two tetraazaanulene macrocycles that coordinate two Ni^{2+} ions (the largest spheres). The macrocycles are held together by two $-(CH_2)_4-$ molecular links. Note that any atom of a given type binds a certain number of its neighbors. The most important message is: if such structural information offered by the 3-D molecular model were not available, it would not be possible to design and carry out the complex synthesis of the molecule. *Courtesy of Professor B. Korybut-Daszkiewicz.*

would more or less stop. A radical approach in science, even if more rigorous, is very often less fruitful or fertile. Science needs models, simpler than reality but capturing the essence of it, which direct human thought toward much more fertile regions.

The adiabatic approximation offers a *simple 3-D model* of a molecule–an extremely useful concept with great interpretative potential.

In later chapters of this book, this model will gradually be enriched by introducing the notion of chemical bonds between *some* atoms, angles between consecutive chemical bonds, electronic lone pairs, electronic pairs that form the chemical bonds, etc. Such a model inspires our imagination (. . . sometimes too much).[23] This is the foundation of all chemistry, all organic syntheses, conformational analysis, most of spectroscopy, etc. Without this beautiful model, progress in chemistry would be extremely difficult.

6.6 Basic Principles of Electronic, Vibrational, and Rotational Spectroscopy

6.6.1 Vibrational Structure

Equation (6.24) represents the basis of molecular spectroscopy and involves changing the molecular electronic, vibrational, or rotational state of a diatomic molecule. Fig. 6.4 shows an example how the curves $U_k(R)$ [also $E_k^0(R)$] may appear for three electronic states $k = 0, 1, 2$ of a diatomic molecule. Two of these curves ($k = 0, 2$) have a typical for bonding states "hook-like" shape. The third ($k = 1$) is also typical, but for repulsive electronic states.

It was assumed in Fig. 6.4 that $J = 0$ and therefore $V_{kJ}(R) = U_k(R)$. Next, Eq. (6.24) was solved for $U_0(R)$ and a series of solutions $\chi_{kvJ} = \chi_{0v0}$ was found: $\chi_{000}, \chi_{010}, \chi_{020}, \ldots$ with energies $E_{000}, E_{010}, E_{020}, \ldots$, respectively. Then, in a similar way, for $k = 2$, one has obtained

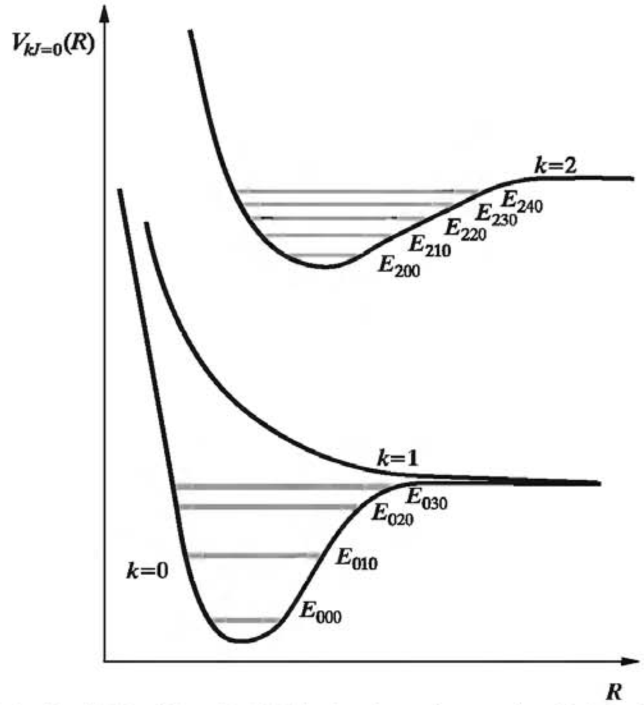

Fig. 6.4. The curves $V_{kJ}(R)$ for $J = 0$ [$V_{k0}(R) = U_k(R)$] for the electronic states $k = 0, 1, 2$ of a diatomic molecule (scheme). The energy levels E_{kvJ} for $J = 0$ corresponding to these curves are also shown. The electronic state $k = 0$ has four, $k = 1$ has zero, and $k = 2$ has five vibrational energy levels.

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[23] We always have to remember that the useful model represents nothing more than a kind of pictorial representation of a more complex and unknown reality.

the series of solutions: $\chi_{200}, \chi_{210}, \chi_{220}, \ldots$ with the corresponding energies $E_{200}, E_{210}, E_{220}, \ldots$ This means that these two electronic levels ($k = 0, 2$) have a *vibrational structure* ($v = 0, 1, 2, \ldots$), the corresponding vibrational levels are shown in Fig. 6.4. Any attempt to find the vibrational levels for the electronic state $k = 1$ would fail.

The pattern of the vibrational levels looks similar to those for the Morse oscillator (p. 192). The low levels are nearly equidistant, reminding us of the results for the harmonic oscillator. The corresponding wave functions also resemble those for the harmonic oscillator. Higher-energy vibrational levels are getting closer and closer, as for the Morse potential. This is a consequence of the anharmonicity of the potential–we are just approaching the dissociation limit where the $U_k(R)$ curves differ qualitatively from the harmonic potential.

6.6.2 Rotational Structure

What would happen if we took $J = 1$ instead of $J = 0$? This corresponds to the potential energy curves $V_{kJ}(R) = U_k(R) + J(J+1)\hbar^2/(2\mu R^2)$, which in our case is $V_{k1}(R) = U_k(R) + 1(1+1)\hbar^2/(2\mu R^2) = U_k(R) + \hbar^2/(\mu R^2)$ for $k = 0, 1, 2$. The new curves therefore represent the old curves plus the term $\hbar^2/(\mu R^2)$, which is the same for all the curves. This corresponds to a *small* modification of the curves for large R and a *larger* modification for small R (see Fig. 6.5). The potential energy curves just go up a little bit on the left.[24] Of course, this is why the solution of Eq. (6.24) for these new curves will be similar to that which we had before; but this tiny shift upward will result in a tiny shift upward of all the computed vibrational levels. Therefore, the levels E_{kv1} for $v = 0, 1, 2, \ldots$ will be a little higher than the corresponding E_{kv0} for $v = 0, 1, 2, \ldots$ (this pertains to $k = 0, 2$, there will be no vibrational states for $k = 1$). This means that each vibrational level v will have its own *rotational structure* corresponding to $J = 0, 1, 2, \ldots$.

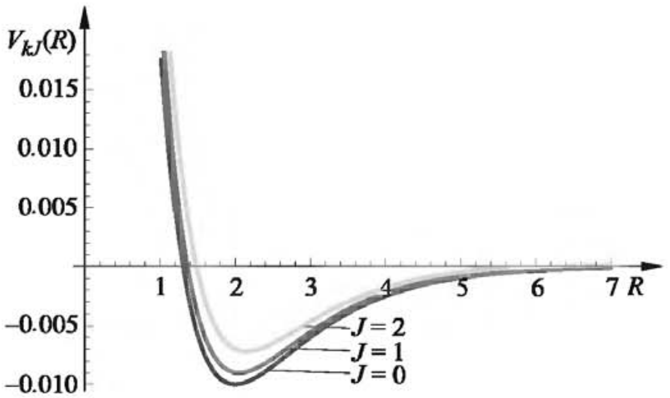

Fig. 6.5. Potential energy curves in arbitrary units corresponding to a diatomic [$V_{kJ}(R)$, k is the electronic state quantum number] for the rotational quantum numbers $J = 0, 1, 2$. One can see the bond weakening under rotational excitation.

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[24] With an accompanying small shift to the right the position of the minimum.

Increasing J means that the potential energy curve becomes shallower[25] At some lower Js the molecule may accommodate all or part of the vibrational levels that exist for $J = 0$. It may happen that after a high-energy rotational excitation (to a large J), the potential energy curve will be so shallow that no vibrational energy level will be possible. This means that the molecule will undergo dissociation due to the excessive centrifugal force.

Separation Between Energy Levels

For molecules other than hydrides, the separation between rotational levels $(E_{kvJ+1} - E_{kvJ})$ is smaller by two to three orders of magnitude than the separation between vibrational levels $(E_{k,v+1,J} - E_{kvJ})$, and the latter is smaller by one or two orders of magnitude when compared to the separation of the electronic levels $(E_{k+1,v,J} - E_{kvJ})$.

This is why electronic excitation corresponds to the absorption of UV or visible light, vibrational excitation to the absorption of infrared radiation, and rotational excitation to the absorption of microwave radiation.

This is what is used in a microwave oven. Food (such as chicken) on a ceramic plate is irradiated by microwaves. This causes rotational excitation of the water molecules[26] that are always present in food. The "rotating" water molecules cause a transfer of kinetic energy to protein, similar to what would happen in traditional cooking. After removing the food from the microwave, the chicken is hot, but the plate is cool (as there is nothing to rotate in the material that makes it up).

In practice, we always have to do with the absorption or emission spectra of a specimen from which we are trying to deduce the relative positions of the energy levels of the molecules involved. We may conclude that in theoretical spectra computed in the center-of-mass system, there will be allowed and forbidden energy intervals.[27] There is no energy levels corresponding to bound states in the forbidden intervals.[28] In the allowed intervals, any region corresponds to an electronic state, whose levels exhibit a pattern (i.e., clustering into vibrational series: one cluster corresponding to $v = 0$, the second to $v = 1$, etc.). Within any cluster, we have rotational levels corresponding to $J = 0, 1, 2, \ldots$ This follows from the fact that the distances between the levels with different k are large, with different v are smaller, and with different J are even smaller.

---

[25] The curve $V_{kJ}(R)$ becomes shallower and the system gets less stable, but for small J, the force constant paradoxically (the second derivative at minimum, if any) *increases*; i.e., the system becomes stiffer due to rotation. Indeed, the second derivative of the rotational energy is equal to $J(J+1)\frac{3\hbar^2}{\mu R^4} > 0$ and, if the position of the minimum of the new curve shifted only a bit (J not too large) with respect to the position of the minimum of $U_k(R)$, the force constant would increase due to the rotational excitation.

[26] Such rotation is somewhat hindered in the solid phase.

[27] In a space-fixed coordinate system (see p. e93), we always are dealing with a continuum of states (due to translations, see p. 69).

[28] The non-bound states densely fill the total energy scale above the dissociation limit of the ground state.

6.7 Approximate Separation of Rotations and Vibrations

Vibrations cannot be exactly separated from rotations for a very simple reason. During vibrations, the length R of the molecule changes, which makes the moment of inertia $I = \mu R^2$ change and influences the rotation of the molecule[29] according to Eq. (6.25).

The separation is feasible only when making an approximation (e.g., when assuming the mean value of the moment of inertia instead of the moment itself). Such a mean value is close to $I = \mu R_e^2$, where R_e stands for the position of the minimum of the potential energy V_{k0}. So we may decide to accept the potential [Eq. (6.25)] for the vibrations in the approximate form[30]:

$$V_{kJ}(R) \approx U_k(R) + J(J+1)\frac{\hbar^2}{2\mu R_e^2}.$$

Since the last term is a constant, this immediately gives the separation of the rotations from the vibrational Eq. (6.24):

$$\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + U_k(R)\right)\chi_{kvJ}(R) = E'\chi_{kvJ}(R), \tag{6.28}$$

where the constant

$$\begin{aligned} E' &= E_{kvJ} - E_{rot}(J), \\ E_{rot}(J) &= J(J+1)\frac{\hbar^2}{2\mu R_e^2}. \end{aligned} \tag{6.29}$$

Now, we may always write the potential $U_k(R)$ as a number $U_k(R_e)$ plus the rest labeled by $V_{vibr}(R)$:

$$U_k(R) = U_k\left(R_e\right) + V_{vibr}(R). \tag{6.30}$$

Then, it is appropriate to call $U_k(R_e)$ the electronic energy $E_{el}(k)$ (corresponding to the equilibrium internuclear distance in electronic state k), while the function $V_{vibr}(R)$ stands for the vibrational potential satisfying $V_{vibr}(R_e) = 0$. After introducing this into Eq. (6.28), we obtain the equation for vibrations (in general, anharmonic):

$$\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + V_{vibr}(R)\right)\chi_{kvJ}(R) = E_{vibr}(v)\chi_{kvJ}(R),$$

where the constant $E_{vibr}(v) = E' - E_{el}$, hence (after adding the translational energy–recalling that we have separated the center-of-mass motion), we have the final approximation:

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[29] Let us recall the energetic pirouette of a dancer. Her graceful movements, stretching her arms out or aligning them along her body, immediately translate into slow or fast rotational motion.

[30] This looks reasonable for *small* amplitude vibrations only. However, this amplitude becomes larger under rotational excitations. Thus, in principle, R_e should increase if J increases and therefore the rotational energy is lower than shown by the formula.

$$E_{kvJ} \approx E_{trans} + E_{el}\left(k\right) + E_{vibr}\left(v\right) + E_{rot}\left(J\right), \qquad (6.31)$$

where the corresponding quantum numbers are given in parentheses: the electronic (k), the vibrational (v), and the rotational (J).

6.8 Understanding the IR Spectrum: HCl

Assume that we have a diluted gas[31] of HCl and we are testing its optical absorption in the microwave region. It is worth noting that the H atom or the Cl atom by itself has zero absorption in this range of spectrum. The spectrum of the HCl molecules represents a strange sequence of double peaks in a peculiar quasi-periodic order. This means the absorption is a direct result of making a molecule from these atoms. We will have to deal with some relative motion of the two interacting atoms, which will be described by molecular vibrational and rotational states and optical transitions between them (with the electronic state staying the same).

6.8.1 Selection Rules

Not all transitions are allowed. All selection rules stem ultimately from conservation laws.

The conservation of energy law says that only a photon of energy $\hbar\omega$ that fits the difference of energy levels can be absorbed.

This fitting is not enough, however. There also must be a coupling (oscillating with frequency ω) between the electromagnetic field and the system. From the theory of interaction of matter and electromagnetic field, we know that the most important coupling term is equal to $-\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\mathcal{E}} = -(\hat{\mu}_x\mathcal{E}_x + \hat{\mu}_y\mathcal{E}_y + \hat{\mu}_z\mathcal{E}_z)$; cf. p. 97, where $\boldsymbol{\mathcal{E}}$ is the oscillating electric field vector of the electromagnetic field and $\hat{\boldsymbol{\mu}}$ is the dipole moment operator. We will assume that the electromagnetic wave propagates along the z-axis; therefore, $\mathcal{E}_z = 0$ and only $\hat{\mu}_x$ and $\hat{\mu}_y$ will count. The quantity $\boldsymbol{\mathcal{E}}$ provides the necessary oscillations in time, while the absorption is measured by $|c|^2$ with $c = \langle\Psi_k|\hat{\boldsymbol{\mu}}(\boldsymbol{r}, \mathbf{R})\Psi_{k'}\rangle_{e,n}$, the coupling between the initial electronic rovibrational state $\Psi_k(\boldsymbol{r}, R) = \psi_k(\boldsymbol{r}; \mathbf{R}) f_k(\boldsymbol{R}) = \psi_{k=0}(\boldsymbol{r}; \mathbf{R})\chi_{v=0}(R)Y_J^M(\theta, \phi)$, and the final electronic rovibrational state $\Psi_{k'}(\boldsymbol{r}, R) = \psi_{k'=0}(\boldsymbol{r}; \mathbf{R})\chi_{v'}(R)Y_{J'}^{M'}(\theta, \phi)$. Where we decided to be within the ground electronic state ($k = k' = 0$) and start from the ground vibrational state ($v = 0$), the symbol $\langle|\rangle_{e,n}$ denotes the integration over the coordinates

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[31] No intermolecular interaction will be assumed.

of all the electrons ("*e*") and nuclei ("*n*").[32] We will integrate first within $c = \langle \Psi_k | \hat{\boldsymbol{\mu}} \Psi_{k'} \rangle_{e,n}$ over electronic coordinates: $\langle \psi_0(\boldsymbol{r};\mathbf{R}) | \hat{\boldsymbol{\mu}}(\boldsymbol{r},\mathbf{R}) \psi_0(\boldsymbol{r};\mathbf{R}) \rangle_e \equiv \boldsymbol{\mu}_{00}(\mathbf{R})$ and get $c = \left\langle \chi_{v=0}(R) Y_J^M(\theta,\phi) | \boldsymbol{\mu}_{00}(\mathbf{R}) \chi_{v'}(R) Y_{J'}^{M'}(\theta,\phi) \right\rangle_n$. The quantity $\boldsymbol{\mu}_{00}(\mathbf{R})$ is the dipole moment of the molecule in the ground electronic state and oriented in space along $\mathbf{R}$.

In case $\boldsymbol{\mu}_{00}(\mathbf{R}) = \mathbf{0}$ (also in case $\boldsymbol{\mu}_{00}(\mathbf{R}) \cdot \boldsymbol{\mathcal{E}} = 0$ for any $\mathbf{R}$), there will be no absorption. Thus, to get a nonzero absorption in rotational and vibrational (microwave or IR) spectra, one has to do with polar molecules, at least for certain $\mathbf{R}$. Therefore, all homonuclear diatomics, although they have a rich structure of rovibrational levels, are unable to absorb electromagnetic radiation in the microwave as well as in the IR range.

A vector in 3-D space may be defined in a Cartesian coordinate system by giving the x, y, and z components, but also in the spherical coordinate system by giving R, θ, ϕ polar coordinates. Now, let us write the dipole moment $\boldsymbol{\mu}_{00}(\mathbf{R})$ in spherical coordinates[33]: $\boldsymbol{\mu}_{00}(\mathbf{R}) = \sqrt{\frac{8\pi}{3}} \mu_{00}(R) Y_1^m(\theta,\phi)$ (see p. e169) with $m = \pm 1, m = 0$ is excluded because it represents $\boldsymbol{\mu}_{00,z} = 0$, which is irrelevant in view of $\mathcal{E}_z = 0$ (there is no coupling in such a case). Thus,

$$c = \left\langle \chi_{v=0}(R) Y_J^M(\theta,\phi) | \boldsymbol{\mu}_{00}(\boldsymbol{R}) \chi_{v'}(R) Y_{J'}^{M'}(\theta,\phi) \right\rangle_n$$
$$= \sqrt{\frac{8\pi}{3}} \langle \chi_0(R) | \mu_{00}(R) \chi_{v'}(R) \rangle_R \left\langle Y_J^M | Y_1^m Y_{J'}^{M'} \right\rangle_{\theta,\phi},$$

where at each integral we have indicated the coordinates to integrate over. Now, introducing the equilibrium internuclear distance R_e (the position of the minimum of the potential energy curve) and the displacement $Q = R - R_e$, as well as expanding $\mu_{00}(R)$ in the Taylor series: $\mu_{00}(R) = \mu_{00}(R_e) + \left(\frac{\partial \mu_{00}}{\partial R}\right)_{R=R_e} Q + \ldots$ and neglecting the higher terms denoted as $+\ldots$

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[32] When describing the electronic function, we have put explicitly the position in space of the nuclei $(\mathbf{R})$ instead of the usual notation with R (which does not tell us how the nuclear axis is oriented in space).

[33]

$$\mu^{(10)} = qR\sqrt{\frac{4\pi}{3}} Y_1^0 = \mu(R)\sqrt{\frac{4\pi}{3}} Y_1^0,$$
$$\mu^{(1,\pm 1)} = \mu(R)\sqrt{\frac{8\pi}{3}} Y_1^{\pm 1}.$$

one obtains:

$$
\begin{aligned}
c = & \sqrt{\frac{8\pi}{3}} \left[\mu_{00}(R_e) \left\langle \chi_0(R) | \chi_{v'}(R) \right\rangle_R + \left(\frac{\partial \mu_{00}}{\partial R} \right)_{R=R_e} \left\langle \chi_0(R) | Q \chi_{v'}(R) \right\rangle_R \right] \\
& \times \left\langle Y_J^M | Y_1^m Y_{J'}^{M'} \right\rangle_{\theta,\phi} = 0 \\
& + \sqrt{\frac{8\pi}{3}} \left(\frac{\partial \mu_{00}}{\partial R} \right)_{R=R_e} \left\langle \chi_0(R) | Q \chi_{v'}(R) \right\rangle_R \left\langle Y_J^M | Y_1^{\pm 1} Y_{J'}^{M'} \right\rangle_{\theta,\phi} .
\end{aligned}
$$

There is only one such wave function $\chi_{v'}$ of the harmonic oscillator, for which $\langle \chi_0(R) | Q \chi_{v'}(R) \rangle_R \neq 0$: it happens only for[34] $v' = 1$.

> We obtain the selection rule for the IR spectroscopy: it is necessary that during the vibration, the dipole moment changes. The main effect of the IR absorption from the $v = 0$ state is that the vibrational quantum number has to change from 0 to 1.

The integral $\left\langle Y_J^M | Y_1^{\pm 1} Y_{J'}^{M'} \right\rangle_{\theta,\phi}$ is nonzero only if[35] $M' = M - m$, $J' = J \pm 1$. This integral has to do with conservation of the total angular momentum and with the conservation of the parity of the system. Any photon has the spin quantum number[36] $s = 1$ (cf. p. 26), which means that besides its energy, it carries the angular momentum: $\hbar$ or $-\hbar$ (right or left circular polarizations of the photon, the electric field $\boldsymbol{\mathcal{E}}$ rotating within the xy plane). After absorption the photon disappears, but it does not matter: the total angular momentum has to be conserved whatever happens. Therefore, the total system: molecule+photon, before as well as after absorption, has to have the total angular momentum with the quantum number equal to[37] $|J - s|$, J, $J + s$ i.e., $J - 1$, J, $J + 1$. The second possibility (with J) would mean that in the IR spectroscopy, the violation of parity occurs.[38] Indeed, the parity of Y_J^M is equal[39] to $(-1)^J$. Therefore, the case $J' = J$ in view of parity of $Y_1^{\pm 1}$ would mean that this is an odd function to integrate, which would make the integral equal to zero.[40] Thus,

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[34] Simply, $Q\chi_0(R)$ is proportional to the Hermite polynomial H_1; i.e., is proportional to $\chi_1(R)$. Due to the orthonormal character of all χ_v, this gives $v = 1$ as the only possibility.

[35] The rule $M' = M - m$ follows from $\int_0^{2\pi} \exp[i(-M + m + M')\phi] d\phi = 2\pi \delta_{M', M-m}$.

[36] With two polarizations: $m_s = 1$ or $m_s = -1$, the polarization $m_s = 0$ is excluded due to the zero mass.

[37] We will describe this problem of quantum-mechanical adding of two angular momenta in a more general way on p. 343.

[38] The conservation of parity is violated in nature, but this effect is much too small to be seen in the analyzed spectrum.

[39] Recall the s,p,d,... orbitals of the hydrogen atom. They correspond to Y_l^m, $l = 0, 1, 2, \ldots$, respectively, and they are of even ($l = 0, 2$) or odd parity ($l = 1$).

[40] This is why we do not have the peak ("missing"): $v = 0$, $J = 0 \to v = 1$, $J = 0$.

the selection rule for the IR and for the microwave spectroscopy reads as:
No photon absorption can happen unless $\Delta J = \pm 1$.

6.8.2 Microwave Spectrum Gives the Internuclear Distance

The lowest energy needed to excite the system would be achieved by changing J only; the related frequencies (for transitions that are allowed by selection rules[41]: $kvJ = 00J \rightarrow 00(J+1)$, $J = 0, 1, 2, \ldots$) are in the range of microwaves. From Eq. (6.29), we get the theoretical estimation of the transition energy $h\nu = hc\bar{\nu} = (J+1)(J+2)\frac{\hbar^2}{2\mu R_e^2} - J(J+1)\frac{\hbar^2}{2\mu R_e^2} = 2(J+1)\frac{\hbar^2}{2\mu R_e^2} = (J+1)2B$. Using the recorded microwave spectrum, we may estimate from this formula the equilibrium interatomic distance for HCl. For the consecutive J, we get 1.29 Å, independently of J (not too large though)[42]. Thus, from the microwave spectrum of HCl, we can read the "interatomic distance." We may compare this distance with, say, the position of minimum of the computed potential energy curve $U_0(R_e)$ of Eq. (6.30).

6.8.3 IR Spectrum and Isotopic Effect

What about the IR region? Fig. 6.6a gives the recorded absorption.

First, why are there these strange doublets in the IR spectrum for HCl? Well, the reason is quite trivial: two natural chlorine isotopes: ^{35}Cl and ^{37}Cl, which are always present in the natural specimen (with proportion 3:1). The H^{35}Cl molecule rotates (as well as oscillates) differently than the H^{37}Cl because of the reduced mass difference [see Eq. (6.29)]. This difference of μ is very small, since what decides in μ is the small mass of the proton[43]. Thus, these two molecules will correspond to two spectra that are similar, but shifted a bit with respect to one another on the frequency axis, the heavier isotope spectrum corresponding to a bit lower frequency.

Fig. 6.6a can be understood with the help of Eq. (6.28), which shows us a model of the phenomena taking place. At room temperature, most of the molecules (Boltzmann law) are in their ground electronic and vibrational states ($k = 0$, $v = 0$). IR quanta are unable to change quantum number k, but they have sufficient energy to change v and J quantum numbers. Fig. 6.6a shows what in fact has been recorded. From the transition selection rules (see above), we have $\Delta v = 1 - 0 = 1$ and either the transitions of the kind $\Delta J = (J+1) - J = +1$ (what is known as the *R branch*, right side of the spectrum) or of the kind $\Delta J = J - (J+1) = -1$ (the *P branch*, left side).

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[41] For more about this, see Appendix C available at booksite.elsevier.com/978-0-444-59436-5.

[42] This is because the minimum of the potential energy curve V_{0J} shifts for large J.

[43] The presence of a deuterium-substituted molecule would have much more serious consequences (a larger shift of the spectrum), because what first of all counts for the reduced mass is the light atom. And the reduced mass controls rotation and vibration.

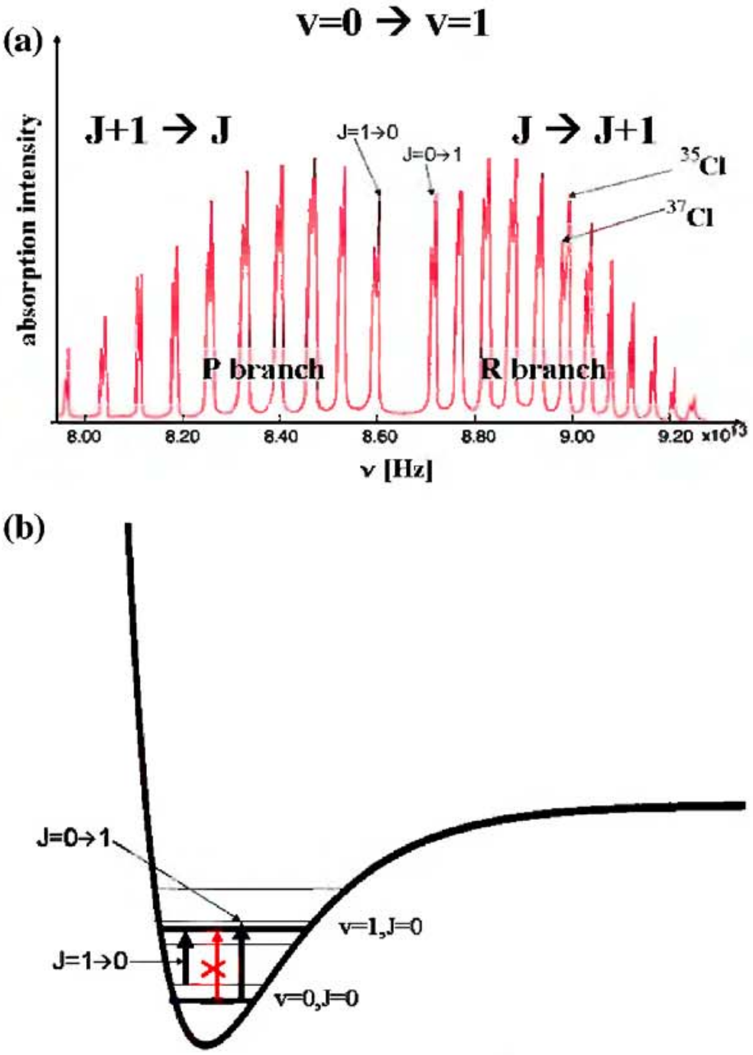

Fig. 6.6. What can we learn about the HCl molecule from its IR spectrum? (a) The IR spectrum (each doublet results from two chlorine isotopes: ^{35}Cl and ^{37}Cl present in the specimen). (b) The central position in the spectrum (between R and P branches) seems to be missing because the transition $v = 0, J = 0 \rightarrow v = 1, J = 0$ is forbidden by the selection rules (as described in the text), and its hypothetical position can be determined with high precision as the mean value of the two transitions shown: $J = 0 \rightarrow J = 1$ and $J = 1 \rightarrow J = 0$. This allows us to compute the force constant of the HCl bond. The energy difference of the same two quanta allows us to estimate the moment of inertia, and therefore the H…Cl distance. Note that the rotational levels corresponding to the vibrational state $v = 1$ are closer to each other than those for $v = 0$. This is due to the wider and wider well and longer and longer equilibrium distance corresponding to the rotationally corrected potential for the motion of the nuclei.

6.8.4 IR Spectrum Gives the Internuclear Distance

The remarkable regularity of the spectrum comes from the fact that the transition energy difference (of the nearest-neighbor peak positions) in a given branch is:

- For the R branch: $E_{excit,J} = h\nu = h\nu_0 + (J+1)(J+2)\frac{\hbar^2}{2\mu R_e^2} - J(J+1)\frac{\hbar^2}{2\mu R_e^2} = h\nu_0 + (J+1)2B$ and $E_{excit,J+1} - E_{excit,J} = (J+2)2B - (J+1)2B = 2B$.

- For the P branch: $E_{excit,J} = h\nu = h\nu_0 + J(J+1)\frac{\hbar^2}{2\mu R_e^2} - (J-1)J\frac{\hbar^2}{2\mu R_e^2} = h\nu_0 + J2B$ and $E_{excit,J} - E_{excit,J-1} = J2B - (J-1)2B = 2B$.

From the known distance $2B$, we can compute the estimation for the equilibrium distance R_e. We see that they are indeed quite equidistant in the spectrum for the R branch and for the P branch separately, but there is a small difference in the Bs for these branches. Is the theory described wrong? No, only our oversimplified theory fails a little. The B for the P branch is a bit larger because the mean interatomic distance gets larger for larger J (due to the centrifugal force).

6.8.5 Why We Have a Spectrum "Envelope"

What about the overall shape of the peaks' intensity ("*the envelope*") of the R and P branches? It looks quite strange: as if the transition from the levels with $v = 0$, $J = 2$ and $v = 0$, $J = 3$ had the largest intensity. Why? The rotational levels are so close that they are significantly populated at a given temperature. In a thermal equilibrium, the population of the levels by HCl molecules is proportional to the degeneracy of the level number J times the Boltzmann factor [i.e., to $p(J;T) = (2J+1)\exp[-\frac{J(J+1)B}{k_BT}]$]. Let us find for which J the probability[44] $p(J;T)$ attains a maximum: $\frac{\mathrm{d}p}{\mathrm{d}J} = 0 = 2\exp[-\frac{J(J+1)B}{k_BT}] - (2J+1)\frac{(2J+1)B}{k_BT}\exp[-\frac{J(J+1)B}{k_BT}]$, which gives for J_{opt} the equation $2 - (2J_{opt}+1)^2\frac{B}{k_BT} = 0$, or $(2J_{opt}+1)^2 = \frac{2k_BT}{B}$. For $T = 300$ K, this gives $J_{opt} = 2.7$; i.e., between $J = 2$ and $J = 3$. It looks as this is just what we see. We may say, therefore, that the spectrum shown has been recorded close to room temperature.

6.8.6 Intensity of Isotopomers' Peaks

One problem still remains. Since the isotopes ^{35}Cl and ^{37}Cl occur with the ratio 3:1, we might expect a similar intensity ratio of the two spectra. Why, therefore, do we have the ratio (Fig. 6.6a) looking as something like 4:3 (for low J)? There are two possible explanations: heavier rotator and heavier oscillator have lower energies and their levels are more populated at nonzero temperatures (however the effect is opposite), and/or this spectrum has too low a resolution, and we are comparing the maxima, while we should be comparing the integral intensity of the peaks (this means the area under the signal recorded). It turns out that in a higher-resolution spectra, for the integral intensities, we indeed see the ratio 3:1.

Thus, we may say that we understand the spectrum of HCl given in Fig. 6.6a.

6.9 A Quasi-Harmonic Approximation

The detailed form of $V_{vibr}(R)$ is obtained from $U_k(R)$ of Eq. (6.30) and therefore from the solution of the Schrödinger Eq. (6.24) with the clamped nuclei Hamiltonian. In principle, there

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[44] It is not normalized to unity, but that does not matter here.

is no other solution but to solve Eq. (6.28) numerically. It is tempting, however, to get an idea of what would happen if a harmonic approximation were applied; i.e., when a harmonic spring was installed between both vibrating atoms. Such a model is very popular when discussing molecular vibrations. There is a unexpected complication though: such a spring cannot exist even in principle. Indeed, even if we constructed a spring that elongates according to Hooke's law, one cannot ensure the same will occur for shrinking. It is true that at the beginning, the spring may fulfill the harmonic law for shrinking as well, but when $R \to 0_+$, the two nuclei just bump into each other and the energy goes to infinity instead of being parabolic. For the spring to be strictly harmonic, we have to admit $R < 0$, which is forbidden because R means a distance. Fig. 6.7 shows the difference between the harmonic potential and the quasi-harmonic approximation for Eq. (6.28).

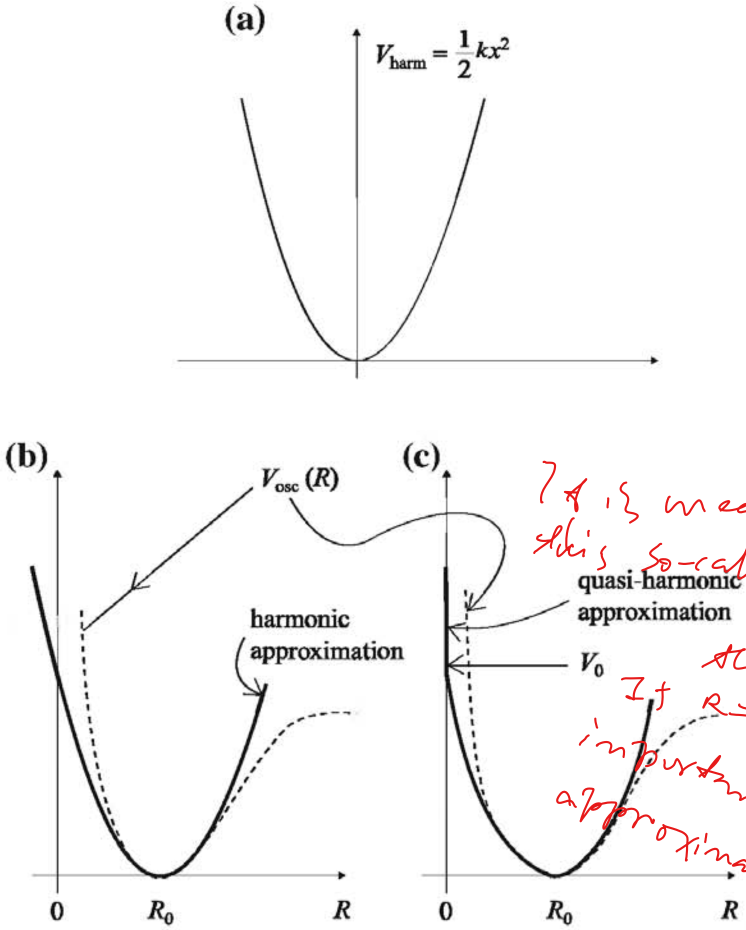

Fig. 6.7. The difference between harmonic and quasi-harmonic approximations for a diatomic molecule. (a) The potential energy for the harmonic oscillator. (b) The harmonic approximation to the oscillator potential $V_{vibr}(R)$ for a diatomic molecule is not realistic since at $R = 0$ (and at $R < 0$), the energy is finite, whereas it should go asymptotically to infinity when R tends to 0. (c) A more realistic (quasi-harmonic) approximation is as follows: the potential is harmonic up to $R = 0$, and for negative R, it goes to infinity. The difference between the harmonic and quasi-harmonic approximations pertains to such high energies (high oscillation amplitudes), that it is practically of negligible importance. In cases b and c, there is a range of small amplitudes where the harmonic approximation is applicable.

It is meaningless to introduce this so-called quasi-harmonic approximation!! If the $R \to 0$ region becomes important, then the harmonic approximation breakdown anyway.

What do we do? Well, sticking to principles is always the best choice.[45] Yet, even in the case of the potential wall shown in Fig. 6.7c, we have an analytical solution.[46] The solution is quite complex, but it gets much simpler assuming $\frac{V_0}{h\nu} \equiv \alpha \gg v$, where $v = 0, 1, 2, \ldots$ stands for the vibrational quantum number that we are going to consider, and $V_0 \equiv V_{vibr}(0)$. This means that we limit ourselves to those vibrational states that are well below V_0. This is quite satisfactory because the hypothetical bump of the two nuclei would occur at vast (even unrealistic) V_0. In such a case, the vibrational energy is equal to $E_v = h\nu\left(v' + \frac{1}{2}\right)$, where the modified "quantum number" $v' = v + \varepsilon_v$ with a tiny modification:

$$\varepsilon_v = \frac{1}{\sqrt{2\pi}} \frac{1}{v!} \left(4\alpha\right)^{v+\frac{1}{2}} \exp\left(-2\alpha\right).$$

The corresponding wave functions very much resemble those of the harmonic oscillator, except that for $R \leq 0$, they are equal to zero. The strictly harmonic approximation results in $\varepsilon_v = 0$, and therefore, $E_v = h\nu\left(v + \frac{1}{2}\right)$; see Chapter 4.

Conclusion: The quasi-harmonic approximation has almost the same result as the (less realistic) harmonic one.

6.10 Polyatomic Molecule

6.10.1 Kinetic Energy Expression

A similar procedure can be carried out for a polyatomic molecule.

Let us consider an SFCS (see Appendix I available at booksite.elsevier.com/978-0-444-59436-5 on p. e93), and vector $\boldsymbol{R}_{CM}$ indicating the center of mass of a molecule composed of M atoms; see Fig. 6.8. Let us construct a Cartesian coordinate system (a body-fixed coordinate system, or BFCS) with the origin in the center of mass and the axes parallel to those of the SFCS (the third possibility in see Appendix I available at booksite.elsevier.com/978-0-444-59436-5).

In the BFCS, an atom α of mass[47] M_α is indicated by the vector $\boldsymbol{r}_\alpha$, its equilibrium position[48] by $\boldsymbol{a}_\alpha$, and the vector of displacement is $\boldsymbol{\xi}_\alpha = \boldsymbol{r}_\alpha - \boldsymbol{a}_\alpha$. If the molecule were rigid and did not rotate in the SFCS, then the velocity of the atom α would be equal to $\boldsymbol{V}_\alpha = \frac{d}{dt}(\boldsymbol{R}_{CM} + \boldsymbol{r}_\alpha) = \dot{\boldsymbol{R}}_{CM}$ (dots mean time derivatives), because the vector $\boldsymbol{r}_\alpha$, indicating the atom from the BFCS, would not change at all. If, in addition, the molecule, still preserving its rigidity, rotated about its center of mass with angular velocity $\boldsymbol{\omega}$ (the vector having the direction of the rotation axis,

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[45] Let me stress once more that the problem appears when making the quasi-harmonic approximation, not in the real system we have.

[46] E. Merzbacher, *Quantum mechanics*, Wiley, New York, 2d edition (1970). The solution we are talking about has to be extracted from a more general problem in this reference. The potential energy used in the reference also has its symmetric counterpart for $R < 0$. Hence, the solution needed here corresponds to the antisymmetric solutions in the more general case (only for such solutions where the wave function is equal to zero for $R = 0$).

[47] What this mass means was discussed earlier in this chapter.

[48] We assume that such a position exists. If there are several equilibrium positions, we just choose one of them.

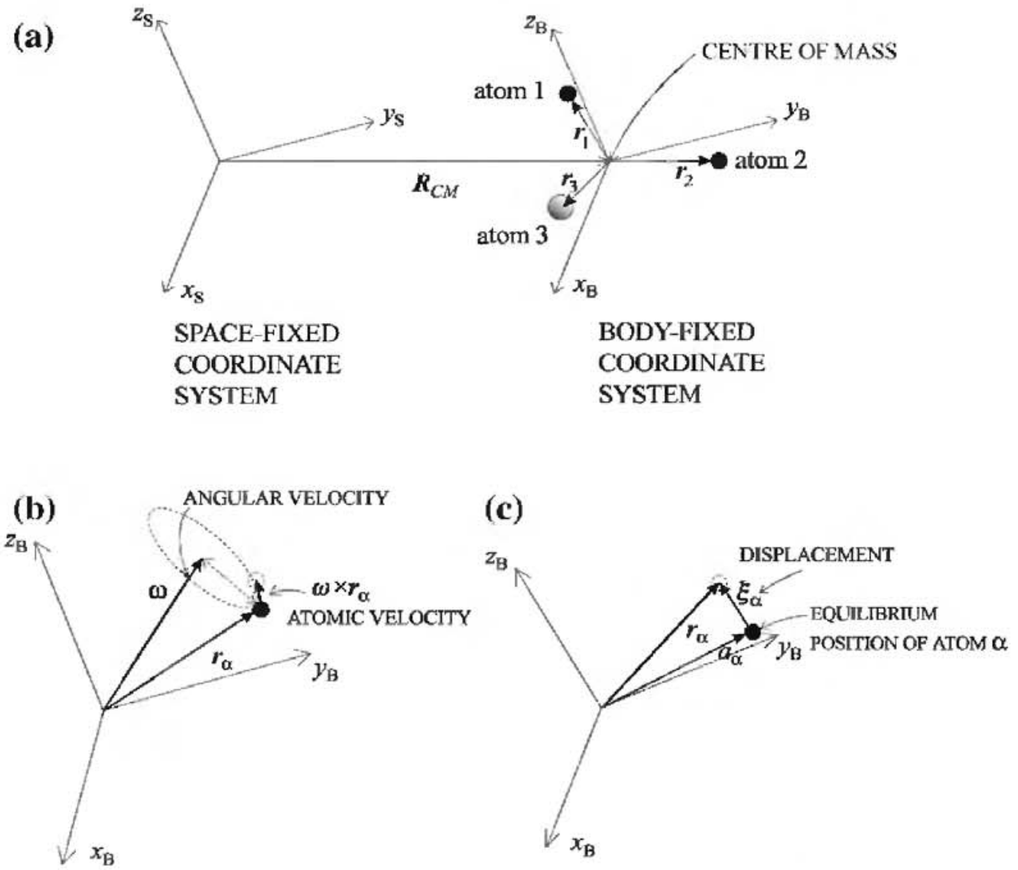

Fig. 6.8. SFCS and BFCS. (a) SFCS is a Cartesian coordinate system arbitrarily chosen in space (left). The origin of the BFCS is located in the center of mass of the molecule (right). The center of mass is shown by the vector $\boldsymbol{R}_{CM}$ from the SFCS. The nuclei of the atoms are indicated by vectors $\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3 \ldots$ from the BFCS. Panel (b) shows what happens to the velocity of atom α, when the system is rotating with the angular velocity given as vector $\boldsymbol{\omega}$. In such a case, the atom acquires additional velocity $\boldsymbol{\omega} \times \boldsymbol{r}_\alpha$. Panel (c) shows that if the molecule vibrates, then atomic positions $\boldsymbol{r}_\alpha$ differ from the equilibrium positions $\boldsymbol{a}_\alpha$ by the displacements $\boldsymbol{\xi}_\alpha$.

right-handed screw orientation, and length equal to the angular velocity in radians per second), then the velocity of the atom α would equal[49] $\boldsymbol{V}_\alpha = \dot{\boldsymbol{R}}_{CM} + (\boldsymbol{\omega} \times \boldsymbol{r}_\alpha)$. However, our molecule is not rigid; everything moves inside it (let us call these motions "vibrations"[50]). Note that no restriction was made yet with respect to the displacements $\boldsymbol{\xi}_\alpha$ - they could be some giant internal motions. Then, the velocity of the atom α with respect to the SFCS is

$$\boldsymbol{V}_\alpha = \dot{\boldsymbol{R}}_{CM} + \left(\boldsymbol{\omega} \times \boldsymbol{r}_\alpha\right) + \dot{\boldsymbol{\xi}}_\alpha. \tag{6.32}$$

---

[49] $|\boldsymbol{\omega} \times \boldsymbol{r}_\alpha| = \omega r_\alpha \sin\theta$, where θ stands for the angle axis/vector $\boldsymbol{r}_\alpha$. If the atom α is on the rotation axis, this term vanishes ($\theta = 0$ or π). In other cases, the rotation radius is equal to $r_\alpha \sin\theta$.

[50] Such a "*vibration*" may mean an vibration of the OH bond, but also a rotation of the $-CH_3$ group or a large displacement of a molecular fragment.

When these velocities V_α are inserted into the kinetic energy T of the molecule calculated in the SFCS, then we get

$$T = \frac{1}{2}\sum_\alpha M_\alpha \left(V_\alpha\right)^2 = \frac{1}{2}\left(\dot{R}_{CM}\right)^2 \sum_\alpha M_\alpha + \frac{1}{2}\sum_\alpha M_\alpha \left(\omega \times r_\alpha\right)^2 + \frac{1}{2}\sum_\alpha M_\alpha \left(\dot{\xi}_\alpha\right)^2$$
$$+ \dot{R}_{CM} \cdot \left[\omega \times \left(\sum_\alpha M_\alpha r_\alpha\right)\right] + \dot{R}_{CM} \cdot \sum_\alpha M_\alpha \dot{\xi}_\alpha + \sum_\alpha M_\alpha \left(\omega \times r_\alpha\right) \cdot \dot{\xi}_\alpha .$$

The first three ("diagonal") terms have a clear interpretation. These are the kinetic energy of the center of mass, the kinetic energy of rotation, and the kinetic energy of vibrations. The last three terms ("non-diagonal") denote the *roto-translational*, *vibro-translational*, and *vibro-rotational couplings*, respectively.

6.10.2 Quasi-Rigid Model–Simplifying by Eckart Conditions

There is a little problem with the expression for the kinetic energy: we have a redundancy in the coordinates. Indeed, we have three coordinates for defining translation (R_{CM}), three that determine rotation (ω), and on top of that M vectors r_α. This is too many: six are redundant. Using such coordinates would be very annoying because we would not be sure whether they are consistent.

We may impose six relations among the coordinates and in this way (if they are correct) get rid of the redundancy. The first three relations are evident because the origin of the BFCS is simply the center of mass. Therefore,

$$\sum_\alpha M_\alpha r_\alpha = \mathbf{0}, \tag{6.33}$$

which as we assume is also true when the atoms occupy equilibrium positions

$$\sum_\alpha M_\alpha a_\alpha = \mathbf{0}.$$

Hence, we obtain a useful relation

$$\sum_\alpha M_\alpha \left(r_\alpha - a_\alpha\right) = \mathbf{0},$$
$$\sum_\alpha M_\alpha \xi_\alpha = \mathbf{0},$$

which, after differentiation with respect to time, becomes

$$\sum_\alpha M_\alpha \dot{\xi}_\alpha = \mathbf{0}. \tag{6.34}$$

If there were several sets of $\boldsymbol{a}_\alpha$'s (i.e., several minima of the potential energy), we would have a problem. This is one of the reasons we need the assumption of the quasi-rigid molecule.

Inserting Eqs. (6.33) and (6.34) into the kinetic energy expression makes the roto-translational and vibro-translational couplings vanish. Thus, we have

$$T = \frac{1}{2}\left(\dot{\boldsymbol{R}}_{CM}\right)^2 \sum_\alpha M_\alpha + \frac{1}{2}\sum_\alpha M_\alpha \left(\boldsymbol{\omega}\times\boldsymbol{r}_\alpha\right)^2 + \frac{1}{2}\sum_\alpha M_\alpha \left(\dot{\boldsymbol{\xi}}_\alpha\right)^2 + \sum_\alpha M_\alpha \left(\boldsymbol{\omega}\times\boldsymbol{r}_\alpha\right)\cdot\dot{\boldsymbol{\xi}}_\alpha .$$

Noting that $\boldsymbol{r}_\alpha = \boldsymbol{a}_\alpha + \boldsymbol{\xi}_\alpha$ and using the relation[51] $(\boldsymbol{A}\times\boldsymbol{B})\cdot\boldsymbol{C} = \boldsymbol{A}\cdot\left(\boldsymbol{B}\times\boldsymbol{C}\right)$, we obtain immediately

$$T = \frac{1}{2}\left(\dot{\boldsymbol{R}}_{CM}\right)^2 \sum_\alpha M_\alpha + \frac{1}{2}\sum_\alpha M_\alpha \left(\boldsymbol{\omega}\times\boldsymbol{r}_\alpha\right)^2 + \frac{1}{2}\sum_\alpha M_\alpha \left(\dot{\boldsymbol{\xi}}_\alpha\right)^2 + \boldsymbol{\omega}\cdot \sum_\alpha M_\alpha \left(\boldsymbol{a}_\alpha\times\dot{\boldsymbol{\xi}}_\alpha\right) + \boldsymbol{\omega}\cdot\sum_\alpha M_\alpha \left(\boldsymbol{\xi}_\alpha\times\dot{\boldsymbol{\xi}}_\alpha\right).$$

We completely get rid of the redundancy if we agree the second *Eckart condition*[52] is introduced (equivalent to three conditions for the coordinates):

$$\sum_\alpha M_\alpha \left(\boldsymbol{a}_\alpha\times\dot{\boldsymbol{\xi}}_\alpha\right) = \boldsymbol{0}. \tag{6.35}$$

The condition means that we do not expect the internal motion to generate any angular momentum.[53] This completes our final expression for the kinetic energy T of a polyatomic quasi-rigid molecule

$$T = T_{trans} + T_{rot} + T_{vibr} + T_{Coriolis}. \tag{6.36}$$

The kinetic energy in an SFCS is composed of:

- The kinetic energy of the center of mass (translational energy), $T_{trans} = \frac{1}{2}\left(\dot{\boldsymbol{R}}_{CM}\right)^2 \sum_\alpha M_\alpha$.
- The rotational energy of the whole molecule, $T_{rot} = \frac{1}{2}\sum_\alpha M_\alpha \left(\boldsymbol{\omega}\times\boldsymbol{r}_\alpha\right)^2$.
- The kinetic energy of the internal motions ("*vibrations*"), $T_{vibr} = \frac{1}{2}\sum_\alpha M_\alpha \left(\dot{\boldsymbol{\xi}}_\alpha\right)^2$.

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[51] These are two ways of calculating the volume of the parallelepiped according to the formula: surface of the base times the height.

[52] Carl Eckart, professor at California Institute of Technology, contributed to the birth of quantum mechanics [e.g., C. Eckart, *Phys. Rev., 28,* 711 (1926)].

[53] The problem is whether indeed we do not generate any momentum by displacing the nuclei from their equilibrium positions. A flexible molecule may have quite a number of different equilibrium positions (see Chapter 7). We cannot expect all of them to satisfy Eq. (6.35), where one of these equilibrium positions is treated as a reference. Eq. (6.35) means that we restrict the molecular vibrations to have only small amplitudes about a single equilibrium position (quasi-rigid model).

- The last term, usually very small, is known as Coriolis energy[54], $T_{Coriolis} = \boldsymbol{\omega}\cdot\sum_\alpha M_\alpha\left(\boldsymbol{\xi}_\alpha \times \dot{\boldsymbol{\xi}}_\alpha\right)$. It couples the internal motions ("*vibrations*") within the molecule with its rotation.

After the Eckart conditions are introduced, all the coordinates (i.e., the components of the vectors $\boldsymbol{R}_{CM}$, $\boldsymbol{\omega}$ and all $\boldsymbol{\xi}_\alpha$), can be treated as independent.

6.10.3 Approximation: Decoupling of Rotation and Vibration

Since the Coriolis term is small, in the first approximation we may decide to neglect it. Also, when assuming small vibrational amplitudes $\boldsymbol{\xi}_\alpha$, which is a reasonable approximation in most cases, we may replace $\boldsymbol{r}_\alpha$ by the corresponding equilibrium positions $\boldsymbol{a}_\alpha$ in the rotational term of Eq. (6.35): $\sum_\alpha M_\alpha(\boldsymbol{\omega}\times\boldsymbol{r}_\alpha)^2 \approx \sum_\alpha M_\alpha(\boldsymbol{\omega}\times\boldsymbol{a}_\alpha)^2$, in full analogy with Eq. (6.29). After these two approximations have been made, the kinetic energy represents the sum of the three independent terms (i.e., each depending on different variables)

$$T \approx T_{trans} + T_{rot} + T_{vibr} \tag{6.37}$$

with $T_{rot} \approx \frac{1}{2}\sum_\alpha M_\alpha(\boldsymbol{\omega}\times\boldsymbol{a}_\alpha)^2$.

6.10.4 Spherical, Symmetric, and Asymmetric Tops

Equation (6.37) may serve to construct the corresponding kinetic energy operator for a polyatomic molecule. There is no problem (see Chapter 1) with the translational term: $-\frac{\hbar^2}{2\sum_\alpha M_\alpha}\Delta_{\boldsymbol{R}_{CM}}$; the vibrational term will be treated in Chapter 7, p. 355.

There is a problem with the rotational term. A rigid body (the equilibrium atomic positions $\boldsymbol{a}_\alpha$ are used), such as the benzene molecule, rotates, but due to symmetry, it may have some special axes characterizing the *moments of inertia*. The moment of inertia represents a tensor of rank 3 with the following components:

$$\left\{\begin{array}{lll} \sum_\alpha M_\alpha(a_{y,\alpha}^2 + a_{z,\alpha}^2) & \sum_\alpha M_\alpha a_{x,\alpha}a_{y,\alpha} & \sum_\alpha M_\alpha a_{x,\alpha}a_{z,\alpha} \\ \sum_\alpha M_\alpha a_{x,\alpha}a_{y,\alpha} & \sum_\alpha M_\alpha(a_{x,\alpha}^2 + a_{z,\alpha}^2) & \sum_\alpha M_\alpha a_{y,\alpha}a_{z,\alpha} \\ \sum_\alpha M_\alpha a_{x,\alpha}a_{z,\alpha} & \sum_\alpha M_\alpha a_{y,\alpha}a_{z,\alpha} & \sum_\alpha M_\alpha(a_{x,\alpha}^2 + a_{y,\alpha}^2) \end{array}\right\},$$

to be computed in the BFCS (see Appendix I available at booksite.elsevier.com/978-0-444-59436-5 on p. e93). The diagonalization of the matrix (see Appendix K available at booksite.elsevier.com/978-0-444-59436-5 on p. e105) corresponds to a certain rotation of the BFCS to a coordinate system rotating with the molecule (RMCS), and gives as the eigenvalues I_{xx}, I_{yy}, I_{zz}.

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[54] Gaspard Gustav de Coriolis (1792 – 1843), was a French engineer and mathematician and director of the Ecole Polytechnique in Paris. In 1835, Coriolis introduced the notion of work, the equivalence of work and energy, and also a coupling of rotation and vibration.

When $I_{xx} = I_{yy} = I_{zz}$, the rotating body is called a *spherical rotator* or a *spherical top* (example: methane molecule); when $I_{xx} = I_{yy} \neq I_{zz}$, it is called a *symmetric top* (examples: benzene, ammonia molecules); when $I_{xx} \neq I_{yy} \neq I_{zz}$, then the top is asymmetric (example: water molecule).

Fig. 6.9 gives four classes of the rotators (tops).

Then, the classical expression for the kinetic energy of rotation takes the form[55]

$$\frac{1}{2}\sum_{\alpha} M_\alpha \left(\boldsymbol{\omega} \times \boldsymbol{a}_\alpha\right)^2 = \frac{1}{2}\left(I_{xx}\omega_x^2 + I_{yy}\omega_y^2 + I_{zz}\omega_z^2\right) = \frac{J_x^2}{2I_{xx}} + \frac{J_y^2}{2I_{yy}} + \frac{J_z^2}{2I_{zz}}, \qquad (6.38)$$

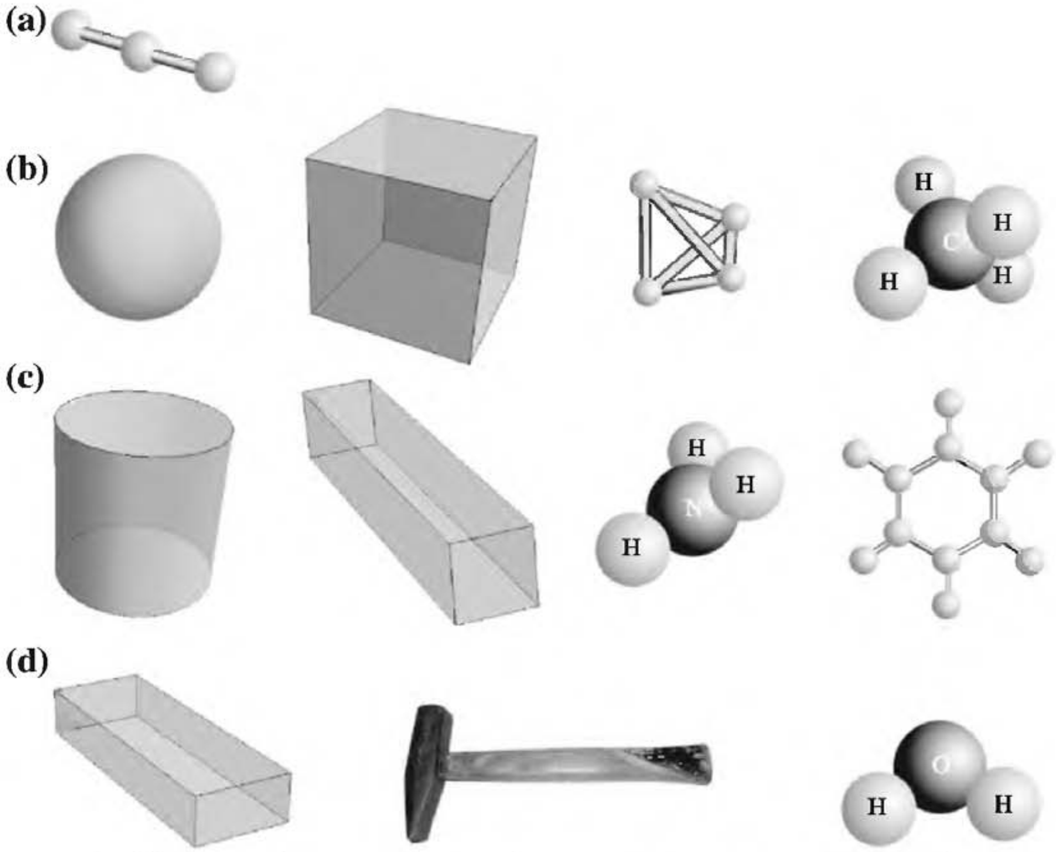

Fig. 6.9. Examples of four classes of tops (rotators). The numbers I_{xx}, I_{yy}, I_{zz} represent the eigenvalues of the tensor of inertia computed in a BFCS. There are four possibilities: (a) a linear rotator ($I_{xx} = I_{yy} = 0$, $I_{zz} \neq 0$); e.g., a diatomic or CO_2 molecule; (b) a spherical rotator ($I_{xx} = I_{yy} = I_{zz}$); e.g., a sphere, a cube, a regular tetrahedron, or a methane molecule; (c) a symmetric rotator ($I_{xx} = I_{yy} \neq I_{zz}$); e.g., a cylinder, a rectangular parallelepiped with square base, ammonia or benzene molecule; (d) an asymmetric rotator ($I_{xx} \neq I_{yy} \neq I_{zz}$); e.g., a general rectangular parallelepiped, a hammer, or water molecule.

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[55] H. Goldstein, *Classical Mechanics*, 2d edition, Addison-Wesley (1980).

where ω_x, ω_y, and ω_z stand for the components of $\boldsymbol{\omega}$ in the RMCS, and J_x, J_y, and J_z represent the components of angular momentum also computed in the RMCS.[56]

It is not straightforward to write down the corresponding kinetic energy operator. The reason is that in the above expression, we have curvilinear coordinates (because of the rotation from BFCS to RMCS[57]), whereas the quantum mechanical operators were introduced only for the Cartesian coordinates (Chapter 1, p. 18). How do we write an operator expressed in some curvilinear coordinates q_i and the corresponding momenta p_i? Boris Podolsky solved this problem,[58] and the result is

$$\hat{T} = \frac{1}{2} g^{-\frac{1}{2}} \hat{\boldsymbol{p}}^T g^{\frac{1}{2}} \boldsymbol{G}^{-1} \hat{\boldsymbol{p}}, \tag{6.39}$$

where $\hat{p}_i = -i\hbar\frac{\partial}{\partial q_i}$, $\boldsymbol{G}$ represents a symmetric matrix (*metric tensor*) of the elements g_{rs}, defined by the square of the length element $ds^2 \equiv \sum_r \sum_s g_{rs} dq_r dq_s$, with $g = \det \boldsymbol{G}$ and g_{rs}(g and all g_{rs} being in general some functions of q_r).

6.10.5 Separation of Translational, Rotational, and Vibrational Motions

Equation (6.39) represents the kinetic energy operator. To obtain the corresponding Hamiltonian, we have to add to this energy the potential energy for the motion of the nuclei, U_k, where k labels the electronic state. The last energy depends uniquely on the variables $\boldsymbol{\xi}_\alpha$ that describe atomic vibrations and corresponds to the electronic energy $U_k(R)$ of Eq. (6.30), except that instead of the variable R, which pertains to the oscillation, we have the components of the vectors $\boldsymbol{\xi}_\alpha$. Then, in full analogy with Eq. (6.30), we may write

$$U_k(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2, \ldots \boldsymbol{\xi}_M) = U_k(\mathbf{0}, \mathbf{0}, \ldots \mathbf{0}) + V_{k,vibr}(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2, \ldots \boldsymbol{\xi}_M),$$

where the number $U_k(\mathbf{0}, \mathbf{0}, \ldots \mathbf{0}) = E_{el}(k)$ may be called the electronic energy in state k, and $V_{k,vibr}(\mathbf{0}, \mathbf{0}, \ldots \mathbf{0}) = 0$.

Since (after the approximations are made) the translational, rotational, and vibrational (internal motion) operators depend on their own variables, after separation the total wave function represents a product of three eigenfunctions (translational, rotational, and vibrational) and the total energy is the sum of the translational, rotational, and vibrational energies [fully analogous with Eq. (6.31)]:

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[56] We recall from classical mechanics that an expression for rotational motion results from the corresponding one for translational motion by replacing mass by moment of inertia, momentum by angular momentum, and velocity by angular velocity. Therefore, the middle part of the above formula for kinetic energy represents an analog of $\frac{mv^2}{2}$ and the last part is an analog of $\frac{p^2}{2m}$.

[57] The rotation is carried out by performing three successive rotations by what are known as Euler angles. For details, see Fig. 14.5, as well as R.N. Zare, *Angular Momentum*, Wiley, New York (1988), p. 78.

[58] B. Podolsky, *Phys. Rev., 32,* 812 (1928).

$$E \approx E_{trans} + E_{el}(k) + E_{rot}(J) + E_{vibr}(v_1, v_2, \ldots v_{3M-6}). \tag{6.40}$$

where k denotes the electronic state, J the rotational quantum number, and v_i are the vibrational quantum numbers that describe the vibrational excitations (in Chapter 7, we will see a harmonic approximation for these oscillations).

6.11 Types of States

6.11.1 Repulsive Potential

If we try to solve Eq. (6.28) for vibrations with a repulsive potential, we would not find any solution of class Q. Among continuous, but non-square-integrable, functions, we would find an infinite number of eigenfunctions, and the corresponding eigenvalues would form a continuum, Fig. 6.10a. These eigenvalues reflect the fact that the system has dissociated and its dissociation products may have any kinetic energy larger than the dissociation limit (i.e., when having dissociated fragments with no kinetic energy). Any collision of two fragments (that correspond to the repulsive electronic state) will finally result in the fragments flying off. Imagine that the two fragments are located at a distance R_0, with corresponding total energy E, and that the system is allowed to relax according to the potential energy shown in Fig. 6.10a. The system slides down the potential energy curve (i.e., the potential energy lowers) and, since the total energy is conserved, its kinetic energy increases accordingly. Finally, the potential energy curve flattens, attaining $E_A + E_B$, where E_A denotes the internal energy of the fragment A (a similar thing happens for B). The final kinetic energy is equal to $E - (E_A + E_B)$ in SFCS.

6.11.2 "Hook-like" Curves

Another typical potential energy curve is shown in Fig. 6.10b and has the shape of a hook. Solving Eq. (6.28) for such a curve usually[59] gives a series of bound states; i.e., with their wave functions (Fig. 6.11) concentrated in a finite region of space and exponentially vanishing on leaving it. Fig. 6.10 shows the three discrete energy levels found and the continuum of states above the dissociation limit, similar to the curve in Fig. 6.10a. The continuum has, in principle, the same origin as before (any kinetic energy of the fragments).

Thus, the overall picture is that a system may have some bound states, but above the dissociation limit, it can also acquire any energy and the corresponding wave functions are non-normalizable (non-square-integrable).

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[59] This applies to a sufficiently deep and wide potential energy well.

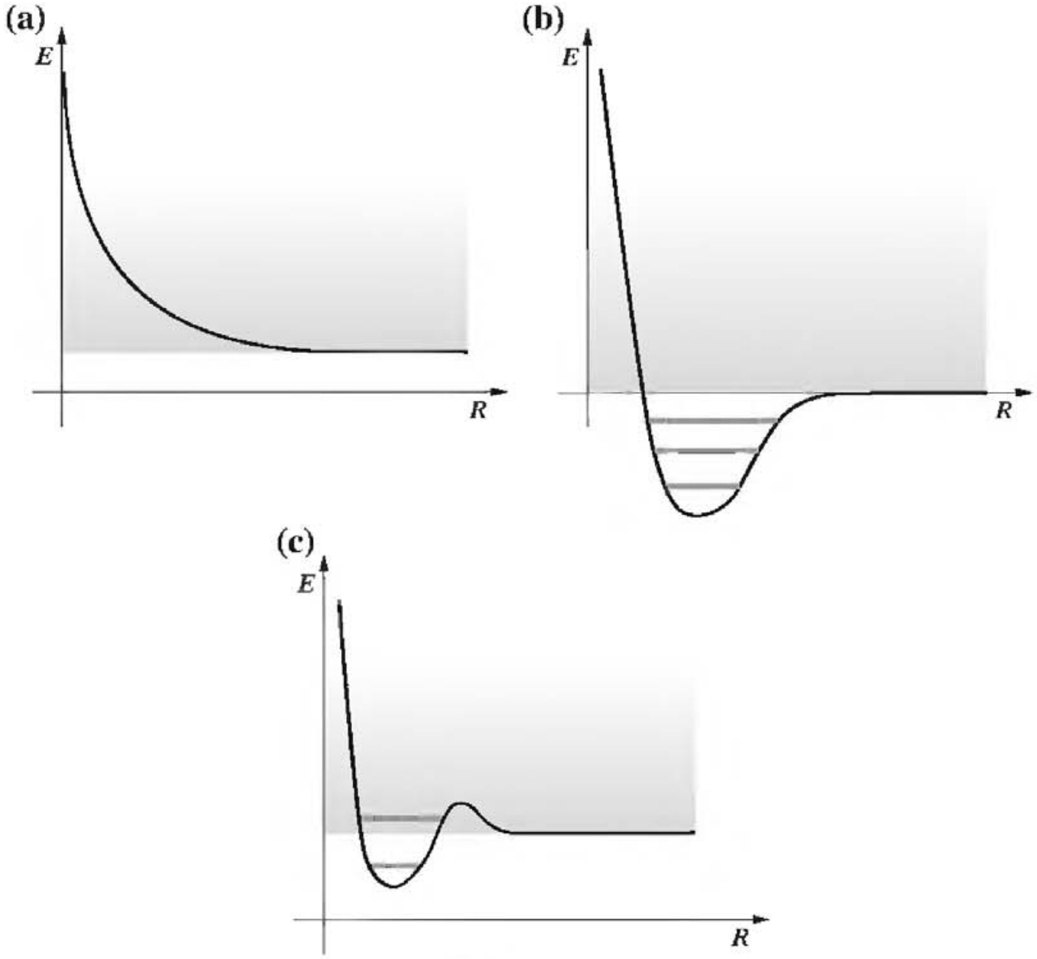

Fig. 6.10. An example of three different electronic states. (a) Repulsive state (no vibrational states, a ball representing the nuclear configuration will slide down resulting in dissociation); (b) three bound vibrational states (the ball will oscillate within the well); (c) one bound vibrational state (the ball oscillates) and one metastable vibrational state (the ball oscillates for some time and then goes to infinity, which means dissociation). A continuum of allowed states (shadowed area) with nonzero kinetic energy of the dissociation products is above the dissociation limit.

6.11.3 Continuum

The continuum may have a quite complex structure. First of all, the number of states per energy unit depends, in general, on the position on the energy scale where this energy unit is located. Thus, the continuum may be characterized by the *density of states* (the number of states per unit energy) as a function of energy. This may cause some confusion because the number of continuum states in any energy section is infinite. The problem is, however, that the infinities differ: some are "more infinite than others." The continuum does not mean a banality of the states involved (Fig. 6.10c). The continuum extends over the dissociation limit, irrespective what kind of potential energy curve one has for finite values of R. In cases similar to that of Fig. 6.10c, the continuum will exist independently of how wide and high the barrier is. But, the barrier

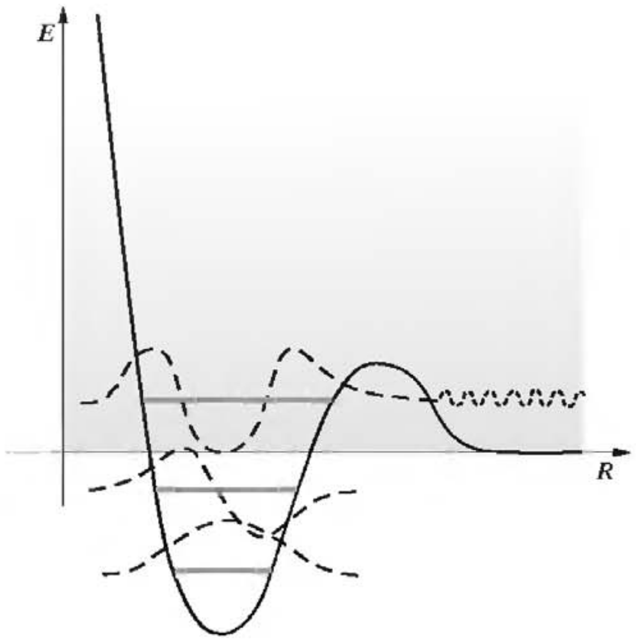

Fig. 6.11. The bound, continuum, and resonance (metastable) states of an anharmonic oscillator. Two discrete bound states are shown (energy levels and wave functions) in the lower part of the image. The continuum (shaded area) extends above the dissociation limit; i.e., the system may have any of the energies above the limit. There is one resonance state in the continuum, which corresponds to the third level in the potential energy well of the oscillator. Within the well, the wave function is very similar to the third state of the harmonic oscillator, but there are differences. One is that the function has some low-amplitude oscillations on the right side. They indicate that the function is non-normalizable and that the system will dissociate sooner or later.

may be so wide that the system will have no idea about any "extra-barrier life," and therefore it will have its "quasi-discrete" states with the energy higher than the dissociation limit. Yet, these states despite its similarity to bound states [illegible] belong to the continuum (are non-normalizable). 邂逅复合物 Such states are metastable and are called *resonances* (cf. p. 182), or *encounter complexes*. The system in a metastable state will sooner or later dissociate, but before this happens it may have a quite successful long life. Fig. 6.11. shows how the metastable and stationary states differ: the metastable ones do not vanish in infinity.

Fig. 6.12 shows what happens to the $V_{kJ}(R)$ curves, if J increases. A simple model potential $U_k(R)$ has been chosen for this illustration. As shown in Fig. 6.12, rotational excitations may lead to a qualitative change of the potential energy curve for the motion of the nuclei. Rotational excitations destabilize the system, but in a specific way. First, they always introduce a barrier for dissociation (*centrifugal barrier*), but despite of that, the dissociation becomes easier due to a large "pushing up" of the well region. Second, by increasing the energy for small distances, the rotational excitations either make some vibrational levels disappear or may change the character of the levels from stationary ones to metastable vibrational states (vibrational resonances in the continuum). Third, as one can see from Fig. 6.12, the equilibrium distance increases upon rotational excitations.

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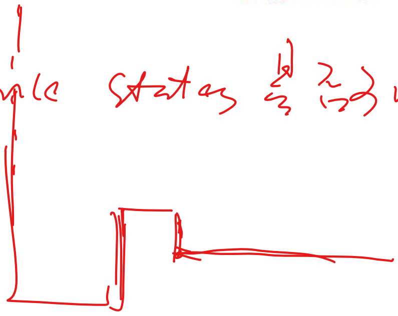

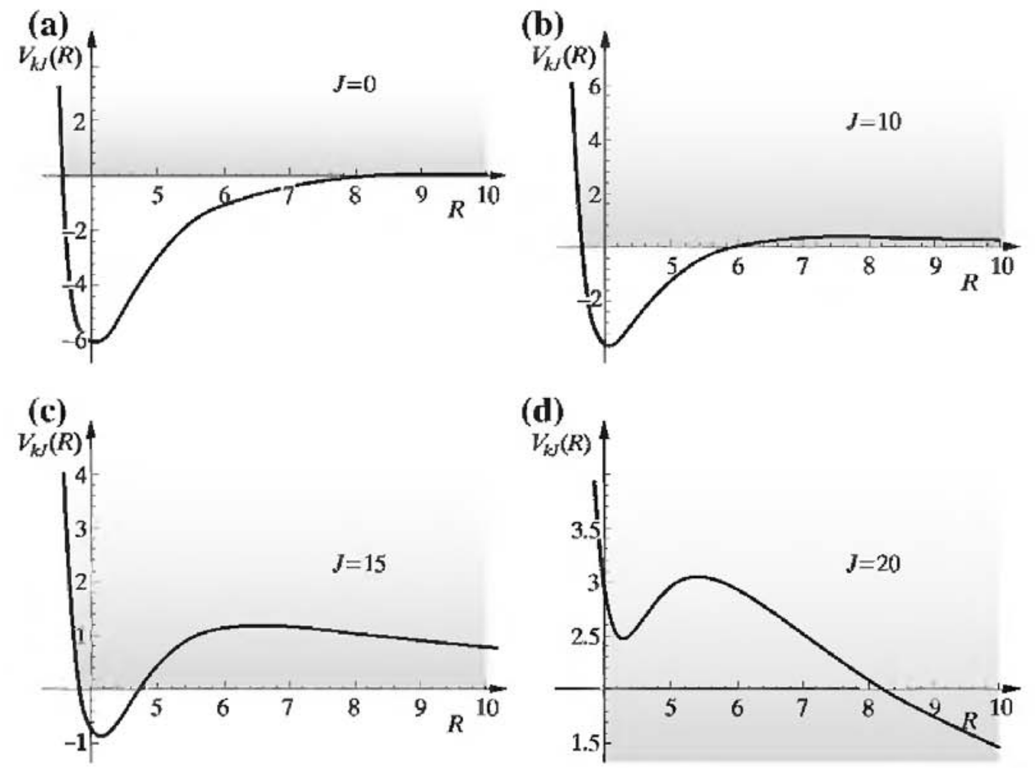

Fig. 6.12. A rotational excitation may lead to creating resonance states. As an illustration, a potential energy curve $V_{kJ}(R)$ has been chosen that resembles what we would see for two water molecules bound by the hydrogen bond. Its first component $U_k(R)$ is taken in the form of the so-called Lennard-Jones potential (cf., p. 347) $U_k(R) = \varepsilon_k \left[\left(\frac{R_{0k}}{R} \right)^{12} - 2 \left(\frac{R_{0k}}{R} \right)^{6} \right]$, with the parameters for the electronic ground state ($k = 0$): $\varepsilon_0 = 6$ kcal/mol and $R_{00} = 4$ a.u. and the corresponding reduced mass $\mu = 16560$ a.u., the parameter ε_0 stands for the well depth, and the R_{00} denotes the position of the well minimum. Panels (a), (b), (c), and (d) correspond to $V_{kJ}(R) = U_k(R) + J(J+1)\hbar^2/(2\mu R^2)$ with $J = 0, 10, 15, 20$, respectively. The larger J is, the shallower the well: the rotation *weakens* the bond, but in a peculiar way. Due to the centrifugal force, the metastable resonance states appear. These are the "normal" vibrational states pushed up by the centrifugal energy beyond the energy of the dissociation limit. For $J = 20$, already *all* states (including the potential resonances) belong to the continuum.

Besides the typical continuum states, which result from the fact that the dissociation products fly slower or faster, one may have also the continuum metastable or resonance states, which resemble the bound states.

The human mind wants to translate such situations into simple pictures, which help us understand what happens. Fig. 6.13 shows an analogy associated with astronomy: the Earth and the Moon are in a bound state and the Earth and an asteroid are in a "primitive," continuum-like state, but if it happens that an asteroid went around the Earth several times and then flew away into space, then one has to do with an analog of a metastable or resonance state (characterized by a finite and nonzero lifetime).

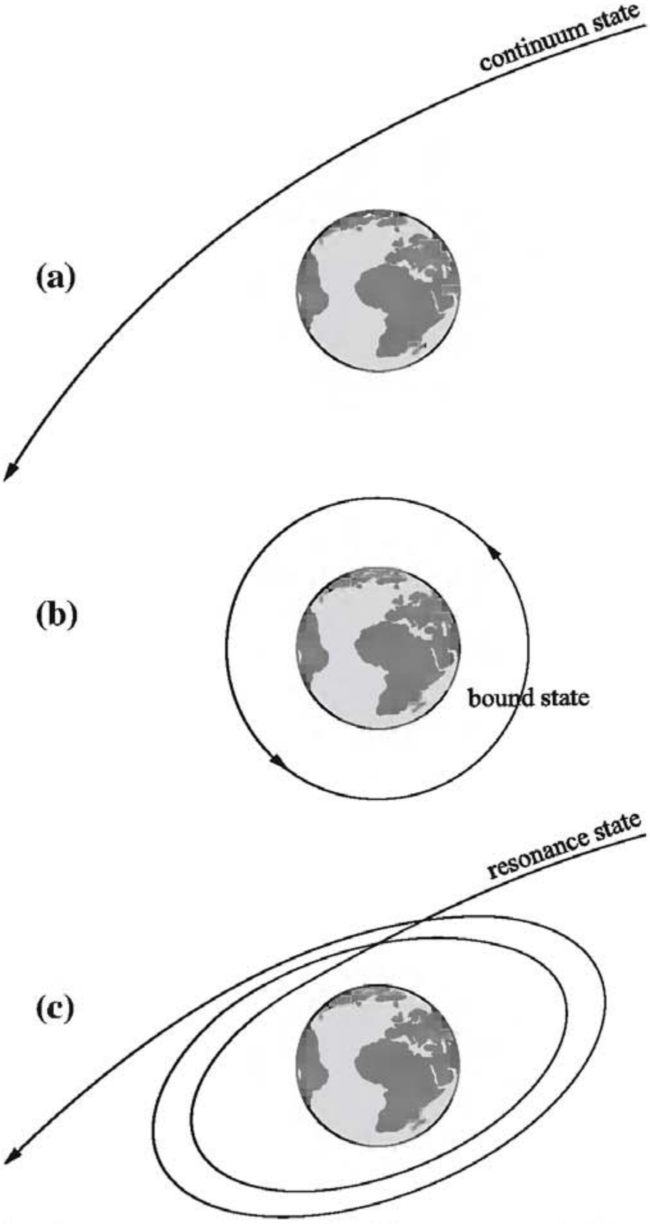

Fig. 6.13. Continuum, bound, and resonance states–an analogy involving the "states" of the Earth and an interacting body. (a) A "primitive" continuum state: an asteroid flies by the Earth and changes trajectory; (b) a bound state: the Moon is orbiting around the Earth; (c) a resonance state: the asteroid was orbiting several times about the Earth and then flew away.

The Schrödinger equation $H\psi = E\psi$ is time-independent; therefore, its solutions do not inform us about the sequence of events, but only about all the possible events with their probability amplitudes.[60] This is why the wave function for the metastable state of Fig. 6.11 exhibits oscillations at large x: they inform us about a *possibility* of dissociation.

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[60] As Einstein said: "*The only reason for time is so that everything does not happen at once.*" The time-independent Schrödinger equation behaves as if "everything would happen at once."

6.11.4 Wave Function "Measurement"

Could we know the vibrational wave function in a given electronic and rotational state? It seemed that such a question could only be answered by quantum mechanical calculations. It turned out,[61] however, that the answer can also come from experimentation. In this experiment, three states are involved: the electronic ground state (G), an electronic excited state M, in particular its vibrational state. This state will be measured, and the third electronic state of a repulsive character (REP) that helps as a detector; see Fig. 6.14.

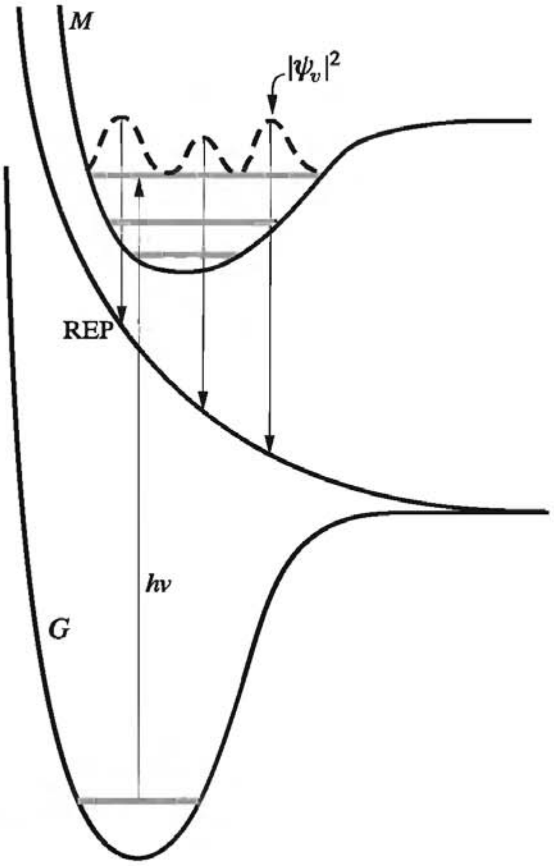

Fig. 6.14. A "measurement" of the wave function ψ_v, or more exactly of the corresponding probability density $|\psi_v|^2$. A molecule is excited from its electronic ground state G to a certain vibrational state ψ_v in the electronic excited state M. From M, the molecule undergoes a fluorescence transition to the state REP. Since the REP state is of repulsive character, the potential energy transforms into kinetic energy (the total energy being preserved). By measuring the kinetic energy of the dissociation products, one is able to calculate their starting potential energy (i.e., how high they were on the REP curve). This enables us to calculate $|\psi_v|^2$.

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[61] W. Koot, P.H.P. Post, W.J. van der Zande, and J. Los, *Zeit. Physik* D, *10*, 233 (1988). The experimental data pertain to the hydrogen molecule.

James Franck (1882–1964), German physicist and professor at the Kaiser Wilhelm Institut für Physikalische Chemie in Berlin, then at the University of Göttingen. Then at John Hopkins University in Baltimore, Maryland, and from 1938 to 1949 at the University of Chicago. Frank also participated in the Manhattan Project. As a freshman at the Department of Law at the University of Heidelberg, he made the acquaintance of the student Max Born. Born persuaded him to resign from his planned career as a lawyer and pursue studies in chemistry, geology, and then physics. In 1914, Franck and his colleague Gustav Hertz used electrons to bombard mercury atoms. The young researchers noted that electrons lose 4.9 eV of their kinetic energy after colliding with mercury atoms. This excess energy is then released by emitting a UV photon. This was the first experimental demonstration that atoms have the electronic energy levels foreseen by Niels Bohr. Both scientists earned the Nobel Prize in 1925 for their work. The fact that, during World War I, Franck was twice decorated with the Iron Cross was the reason that he was one of the few Jews whom the Germans tolerated in academia. Franck, a citizen of the Third Reich, illegally deposited his Nobel Prize medal (with his engraved name) in the Niels Bohr Institute in Copenhagen, Denmark. When in April 1940, the attacking German troops marched through the streets of the Danish capital, George de Hevesy (a future Nobel laureate, 1943) was hiding the golden medal in a strange and very chemical way–he dissolved it in aqua regia. The bottle safely stayed on the shelf the whole occupation period under the nose of the Germans. After the war, the Nobel Committee exchanged the bottle for a new medal for Franck.

?

$e^- + Hg \rightarrow Hg^-$

Edward Condon (1902–1974), American physicist and one of the pioneers of quantum theory in the United States. In 1928, Condon and Gurney discovered the tunneling. More widely known is his second great achievement–the Franck-Condon rule (discussed later in this chapter). During the WW2 he participated in the Manhattan project.

We excite the molecule from the ground vibrational state of G to a certain vibrational state ψ_v of M using a laser. Then the molecule undergoes a spontaneous *fluorescence transition* to REP. The electronic state changes so fast that the nuclei have no time to move (the *Franck-Condon rule*). Whatever falls (vertically, because of the Franck-Condon rule) on the REP state as a result of fluorescence dissociates because this state is repulsive. The kinetic energy of the dissociation products depends on the internuclear distance R when the fluorescence took place (i.e., on the length of the slide the system had down the REP). How often such an R occurs depends on $|\psi_v(R)|^2$. Therefore, investigating the kinetic energy of the dissociation products gives $|\psi_v|^2$.

6.12 Adiabatic, Diabatic, and Non-Adiabatic Approaches

Let us summarize the diabatic, adiabatic, and non-adiabatic concepts, as shown in Fig. 6.15.

Adiabatic case. Suppose that we have a Hamiltonian $\hat{\mathcal{H}}(\boldsymbol{r};\boldsymbol{R})$ that depends on the electronic coordinates $\boldsymbol{r}$ and parametrically depends on the configuration of the nuclei $\boldsymbol{R}$. In practical

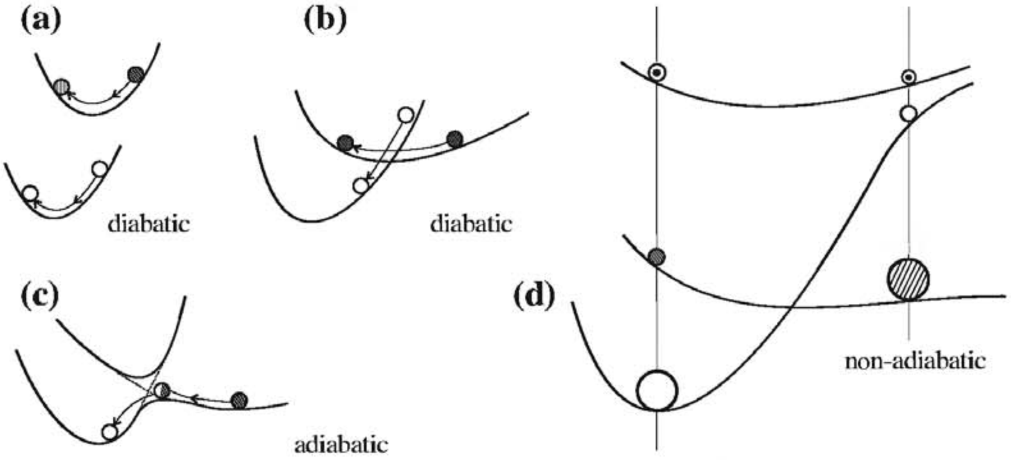

Fig. 6.15. The ~~diabatic,~~ adiabatic, and non-adiabatic approaches to the motion of nuclei (a schematic view). (a) A state that preserves the chemical structure for any molecular geometry is called *diabatic* (e.g., is always ionic, or always covalent). The energies of these states are calculated as the mean values of the clamped nuclei Hamiltonian. In the lower-energy state, the system is represented by a white ball (say, in the ionic state); in the second, the system is represented by the black ball (say, a covalent structure). These balls vibrate all the time in the corresponding wells, preserving the chemical structure. (b) It may happen that two diabatic states cross. If the nuclear motion is fast, the electrons are unable to adjust and the nuclear motion may take place on the diabatic curves (i.e., the bond pattern does not change during this motion). (c) The adiabatic approach, where the diabatic states mix (mainly at a crossing region). Each of the adiabatic states is an eigenfunction of the clamped nuclei Hamiltonian. If the nuclear motion is slow, the electrons are able to adjust to it instantaneously and the system follows the lower adiabatic curve. The bond pattern changes qualitatively during this motion (black ball changes to white ball; e.g., the system undergoes a transition from covalent to ionic). The total wave function is a product of the adiabatic electronic state and a rovibrational wave function. (d) The non-adiabatic approach. In this particular case, three diabatic curves come into play. The total wave function is the sum of three functions (their contributions are geometry-dependent, a larger ball means a larger contribution), each function is a product of a diabatic electronic state times a rovibrational wave function. The system is shown at two geometries. Changing the nuclear geometry, it is as if the system has moved on three diabatic surfaces at the same time. This motion is accompanied by changing the proportions (visualized by the size of the balls) of the electronic diabatic states composing it.

例子有助于区分三种 adiabatic 与 diabatic in context:

applications, most often $\hat{\mathcal{H}}(\boldsymbol{r};\boldsymbol{R}) \equiv \hat{H}_0(\boldsymbol{r};\boldsymbol{R})$, the electronic clamped nuclei Hamiltonian corresponding to Eq. (6.8) and generalized to polyatomic molecules. The eigenfunctions $\psi(\boldsymbol{r};\boldsymbol{R})$ and the eigenvalues $E_i(\boldsymbol{R})$ of the Hamiltonian $\hat{\mathcal{H}}(\boldsymbol{r};\boldsymbol{R})$ are called *adiabatic* (see Fig. 6.15). If we take $\hat{\mathcal{H}} = \hat{H}_0(\boldsymbol{r};\boldsymbol{R})$, then in the adiabatic approximation (p. 268), the total wave function is represented by a product

① adiabatic
vs diabatic state

$$\Psi(\boldsymbol{r},\boldsymbol{R}) = \psi(\boldsymbol{r};\boldsymbol{R})f(\boldsymbol{R}), \tag{6.41}$$

② adiabatic vs diabatic
process (approximation)

where $f(\boldsymbol{R})$ is a rovibrational wave function that describes the rotations and vibrations of the system.

③ adiabatic vs diabatic approach

Diabatic case. Imagine now a basis set $\bar{\psi}_i(\boldsymbol{r};\boldsymbol{R})$, $i = 1, 2, 3, \ldots M$ of some particular electronic wave functions (we will call them *diabatic*) that also depend parametrically on $\boldsymbol{R}$. There are two reasons for considering such a basis set. The first is that we are going to solve the Schrödinger equation $\hat{\mathcal{H}}\Psi_i = E_i\Psi_i$ by using the Ritz method (Chapter 5) and we need a basis set of the expansion functions:

$$\psi(\boldsymbol{r};\boldsymbol{R}) \approx \sum_{i}^{M} c_i \bar{\psi}_i(\boldsymbol{r};\boldsymbol{R}). \tag{6.42}$$

The second reason pertains to chemical interpretation: usually any of the diabatic wave functions are chosen as corresponding to a particular electronic distribution (chemical bond pattern) in the system,[62] and from Eq. (6.42), we may recognize what kind of chemical structure dominates Ψ. Thus, using the diabatic basis, there is a chance of gaining insight into the chemistry going on in the system.[63]

The wave functions $\bar{\psi}_i$ are in general non-orthogonal (we assume them to be normalized). For each of them, we may compute the mean value of the energy (the integration is over the electronic coordinates) as follows:

$$\bar{E}_i(\boldsymbol{R}) = \langle \bar{\psi}_i | \hat{\mathcal{H}}(\boldsymbol{R}) \bar{\psi}_i \rangle, \tag{6.43}$$

and we will call it the *diabatic energy*.

The key point is that we may compare the eigenvalues and eigenfunctions of $\hat{\mathcal{H}}(\boldsymbol{R})$; i.e., the adiabatic states with $\bar{E}_i$ and $\bar{\psi}_i$, respectively. If the diabatic states are chosen in a realistic way, they are supposed to be close to the adiabatic states for most configurations $\boldsymbol{R}$ (see Figs. 6.15a–c). These relations will be discussed shortly.

Non-adiabatic case. The diabatic states or the adiabatic states may be used to construct the basis set for the motion of the electrons *and* nuclei in the non-adiabatic approach. Such a basis function is taken as a product of the electronic (diabatic or adiabatic) wave function and of a rovibrational wave function that depends on $\boldsymbol{R}$. In a non-adiabatic approach, the total wave function is a superposition of these product-like contributions:

$$\Psi(\boldsymbol{r};\boldsymbol{R}) = \sum_{k} \bar{\psi}_k(\boldsymbol{r};\boldsymbol{R}) f_k(\boldsymbol{R}). \tag{6.44}$$

---

[62] Let us take the example of the NaCl molecule: $\bar{\psi}_1$ may describe the ionic $Na^{+}Cl^{-}$ distribution, while $\bar{\psi}_2$ may correspond to the covalent bond Na–Cl. The adiabatic wave function $\psi(\boldsymbol{r};\boldsymbol{R})$ of the NaCl molecule may be taken as a superposition of $\bar{\psi}_1$ and $\bar{\psi}_2$. The valence bond (VB) wave functions (VB structures) described in Chapter 10 may be viewed as diabatic states.

[63] This is very important for chemical reactions, in which a chemical structure undergoes an abrupt change. In chemical reactions, large changes of nuclear configuration are accompanied by motions of electrons; i.e., large changes in the chemical bond pattern [a qualitative change of c_i of Eq. (6.42)]. Such a definition leaves us liberty in the choice of diabatic states. This liberty can be substantially reduced by the following. Let us take two adiabatic states that dissociate to different products, well separated on the energy scale. However, for some reason, the two adiabatic energies are getting closer for some finite values of R. For each value of R, we define a space spanned by the two adiabatic functions for that R. Let us find in this space two normalized functions that maximize the absolute value of the overlap integral with the two dissociation states. These two (usually non-orthogonal) states may be called *diabatic*.

This sum means that in the non-adiabatic approach, the motion of the system involves many potential energy surfaces at the same time (see Fig. 6.15d).

The diabatic and the adiabatic electronic states are simply two choices of the basis set in non-adiabatic calculations. If the sets were complete, the results would be identical. The first choice underlines the importance of the chemical bond pattern and the interplay among such patterns. The second basis set highlights the order of the eigenvalues of $\hat{\mathcal{H}}(\boldsymbol{R})$ (the lower/higher-energy adiabatic state).[64]

6.13 Crossing of Potential Energy Curves for Diatomics

6.13.1 The Non-Crossing Rule

Can the adiabatic curves $E_k^0(R)$ cross when R changes?

To solve this problem in detail, let us limit ourselves to the simplest situation: the two-state model (see Appendix D available at booksite.elsevier.com/978-0-444-59436-5). Let us consider a diatomic molecule and such an internuclear distance R_0 that the two electronic adiabatic states[65] $\psi_1(\boldsymbol{r};R_0)$ and $\psi_2(\boldsymbol{r};R_0)$ correspond to the non-degenerate (but close in the energy scale) eigenvalues of the clamped nuclei Hamiltonian $\hat{H}_0(R_0)$:

$$\hat{H}_0(R_0)\psi_i(\boldsymbol{r};R_0) = E_i(R_0)\psi_i(\boldsymbol{r};R_0),\ i=1,2.$$

Since $\hat{H}_0$ is Hermitian and $E_1 \neq E_2$, we have the orthogonality of $\psi_1(\boldsymbol{r};R_0)$ and $\psi_2(\boldsymbol{r};R_0)$: $\langle\psi_1|\psi_2\rangle = 0$.

Now, we are interested in solving

$$\hat{H}_0(R)\psi(\boldsymbol{r};R) = E\psi(\boldsymbol{r};R)$$

for R in the vicinity of R_0 and ask whether it is possible for the energy eigenvalues to cross. The eigenfunctions of $\hat{H}_0$ will be sought as linear combinations of ψ_1 and ψ_2:

$$\psi(\boldsymbol{r};R) = c_1(R)\psi_1(\boldsymbol{r};R_0) + c_2(R)\psi_2(\boldsymbol{r};R_0). \tag{6.45}$$

Note that for this distance R

$$\hat{H}_0(R) = \hat{H}_0(R_0) + V(R), \tag{6.46}$$

and $V(R)$ is certainly small because R is close to R_0 and $V(R_0)=0$. Using the Ritz method (Chapter 5, see Appendix D, case III), we arrive at two adiabatic solutions, and the corresponding

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[64] In polyatomic systems, there is a serious problem with the adiabatic basis (this is why the diabatic functions are preferred). As we will see later, the adiabatic electronic wave function is multivalued, and the corresponding rovibrational wave function, having to compensate for this (because the total wave function must be single-valued), also has to be multivalued.

[65] These states are adiabatic only for $R=R_0$, but when considering $R \neq R_0$, they may be viewed as diabatic (because they are not the eigenfunctions for that R).

energies read as

$$E_{\pm}(R) = \frac{\bar{E}_1 + \bar{E}_2}{2} \pm \sqrt{\left(\frac{\bar{E}_1 - \bar{E}_2}{2}\right)^2 + |V_{12}|^2}, \tag{6.47}$$

where $V_{ij}(R) \equiv \left\langle \psi_i | \hat{V}(R) \psi_j \right\rangle$ and

$$\bar{E}_i(R) = \left\langle \psi_i(\boldsymbol{r}; R_0) | \hat{H}_0(R) \psi_i(\boldsymbol{r}; R_0) \right\rangle = E_i(R) + V_{ii}(R). \tag{6.48}$$

The crossing of the energy curves at a given R means that $E_+ = E_-$, and from this, it follows that the expression under the square root symbol has to equal zero. Since, however, the expression is the sum of two squares, the crossing needs *two* conditions to be satisfied simultaneously:

$$\bar{E}_1 - \bar{E}_2 = 0, \tag{6.49}$$

$$|V_{12}| = 0. \tag{6.50}$$

Two conditions, and a *single* parameter R to change. If you adjust the parameter to fulfill the first condition, the second one is violated, and vice versa. The crossing $E_+ = E_-$ may occur only when, for some reason; e.g., because of the symmetry, the *coupling constant* is automatically equal to zero, $|V_{12}| = 0$, for all R. Then, we have only a *single* condition to be fulfilled, and it can be satisfied by changing the parameter R; i.e., crossing can occur. The condition $|V_{12}| = 0$ is equivalent to $|H_{12}| \equiv \left\langle \psi_1 | \hat{H}_0(R) \psi_2 \right\rangle = 0$, because $\hat{H}_0(R) = \hat{H}_0(R_0) + \hat{V}$, and $\left\langle \psi_1 | \hat{H}_0(R_0) \psi_2 \right\rangle = 0$ due to the orthogonality of both eigenfunctions of $\hat{H}_0(R_0)$.

Now we will refer to group theory (see Appendix C available at booksite.elsevier.com/978-0-444-59436-5, p. e17). The Hamiltonian represents a fully symmetric object, whereas the wave functions ψ_1 and ψ_2 are not necessarily fully symmetric because they may belong to other irreducible representations of the symmetry group. Therefore, in order to make the integral $|H_{12}| = |V_{12}| = 0$, it is sufficient that ψ_1 and ψ_2 transform according to *different* irreducible representations (have different symmetries).[66] Thus,

> the adiabatic curves cannot cross if the corresponding wave functions have the same symmetry.

What will happen if such curves are heading for something that looks like an inevitable crossing? Such cases are quite characteristic and look like an avoided crossing. The two curves look as if they repel each other and avoid the crossing.

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[66] H_{12} transforms according to the representation being the direct product of three irreducible representations: that of ψ_1, that of ψ_2, and that of $\hat{H}$ (the last is, however, fully symmetric, and therefore, does not count in this direct product). In order to have $H_{12} \neq 0$, this direct product, after decomposition into irreducible representations, has to contain a fully symmetric irreducible representation. This, however, is possible only when ψ_1 and ψ_2 transform according to the same irreducible representation.

If two states of a diatomic molecule correspond to different symmetries, then the corresponding potential energy curves can cross.

6.13.2 Simulating the Harpooning Effect in the NaCl Molecule

Our goal now is to show, in an example, what happens to adiabatic states (eigenstates of $\hat{\mathcal{H}}(R)$), if two diabatic energy curves (mean values of the Hamiltonian with the diabatic functions) do cross. Although we are not aiming at an accurate description of the NaCl molecule (we prefer simplicity and generality), we will try to construct a toy (a model) that mimics this particular system.

The sodium atom has 11 electrons (the electronic configuration[67]: $1s^2 2s^2 2p^6 3s^1$), and the chlorine atom contains 17 electrons ($1s^2 2s^2 2p^6 3s^2 3p^5$). The solution of the Schrödinger equation for 28 electrons is difficult. But we are not looking for trouble. Note that with NaCl, the real star is a single electron that goes from the sodium to the chlorine atom, making Na^+ and Cl^- ions. The ions attract each other by the Coulombic force and form the familiar ionic bond. But there is a problem. What is of lower energy: the two non-interacting atoms Na and Cl or the two non-interacting ions Na^+ and Cl^-? The ionization energy of sodium is $I = 495.8$ kJ/mol $= 0.1888$ a.u., whereas the electron affinity of chlorine is only $A = 349$ kJ/mol $= 0.1329$ a.u. This means that the NaCl molecule in its ground state dissociates into atoms, not ions.

To keep the story simple, let us limit ourselves to the single electron mentioned above.[68] First, let us define the two diabatic states (the basis set) of the system: only the 3s orbital of Na (when the electron resides on Na; we have atoms) denoted by $|3s\rangle$ and the 3p orbital of Cl (when the electron is on Cl; we have ions) $|3p\rangle$. Now, what about the Hamiltonian $\hat{\mathcal{H}}$? Well, a reasonable model Hamiltonian may be taken as[69]

$$\hat{\mathcal{H}}(\boldsymbol{r}; R) = -I\ |3s\rangle\langle 3s| - A\,|3p\rangle\langle 3p| - \frac{1}{R}|3p\rangle\langle 3p| + \exp\left(-R\right).$$

Indeed, the mean values of $\hat{\mathcal{H}}$ in the $|3s\rangle$ and $|3p\rangle$ states are equal to

$$\begin{aligned}\bar{E}_1(R) &\equiv \mathcal{H}_{11} = \left\langle 3s|\hat{\mathcal{H}}(3s)\right\rangle = -I - AS^2 - \frac{1}{R}S^2 + \exp\left(-R\right),\\ \bar{E}_2(R) &\equiv \mathcal{H}_{22} = \left\langle 3p|\hat{\mathcal{H}}(3p)\right\rangle = -IS^2 - A - \frac{1}{R} + \exp\left(-R\right),\end{aligned}$$

where (assuming the diabatic functions to be real) the overlap integral $S \equiv \langle 3s|3p\rangle = \langle 3p|3s\rangle$. First of all, this Hamiltonian gives the correct energy limits $\bar{E}_1(R) = -I$ and $\bar{E}_2(R) = -A$, when $R \to \infty$ (the electron binding energy by the sodium and by the chlorine for dissociation into atoms and ions, respectively), which is already very important. The term $\exp(-R)$

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[67] What these configurations really mean is explained in Chapter 8.

[68] The other electrons in our approach will only influence the numerical values of the interaction parameters.

[69] $\boldsymbol{r}$ stands for the coordinates of the electron, and for the diatomic molecule, R replaces $\boldsymbol{R}$.

mimics the repulsion of the inner shells of both atoms[70] and guarantees that the energies go up (which they should) at $R \to 0$. Note also that the $\bar{E}_1(R)$ and $\bar{E}_2(R)$ curves indeed mimic the approaching Na and Cl, and Na^+ and Cl^-, respectively, because in $\bar{E}_2(R)$, there is a Coulomb term $-\frac{1}{R}$, while in $\bar{E}_1(R)$, such an interaction practically disappears for large R. All this gives us a certain confidence that our Hamiltonian $\hat{\mathcal{H}}$ grasps the most important physical effects for the NaCl molecule. The resulting non-diagonal element of the Hamiltonian reads as:

$$\left\langle 3s|\hat{\mathcal{H}}(3p)\right\rangle \equiv \mathcal{H}_{12} = S\left[-I - A - \frac{1}{R} + \exp\left(-R\right)\right].$$

量纲不对!!

As to S, we could in principle calculate it by taking some approximate atomic orbitals, but our goal is less ambitious than that. Let us simply set $S = R\exp\left(-R/2\right)$. Why? Since $S = \langle 3s|3p\rangle = 0$, if $R \to \infty$ or if $R \to 0$, and $S > 0$ for other values of R, then at least our formula takes care of this. In addition, Figs. 6.16a–b show that such a formula for S also gives a quite reasonable set of diabatic curves $\bar{E}_1(R)$ and $\bar{E}_2(R)$: both curves have a single minimum, the minimum for the ionic curve is at about 5.23 a.u., close to the experimental value of 5.33 a.u., and the binding energy is 0.11 a.u. (0.13 for the adiabatic case, see below), and it is also close to the experimental value of 0.15 a.u. Thus, our model to a reasonable extent resembles the real NaCl molecule.

Our goal is the adiabatic energies computed using the diabatic basis chosen, Eq. (6.42). see Appendix D available at booksite.elsevier.com/978-0-444-59436-5 (general case) gives the eigenvalues [$E_+(R)$ and $E_-(R)$] and the eigenfunctions (ψ_+ and ψ_-). Figs. 6.16c–d, show the adiabatic compared to the diabatic curves. The avoided crossing at about 17.9 a.u. is the most important. If the two atoms begin to approach (shown in light gray in Fig. 6.16a), the energy does not change too much (flat energy curve), but if the ions do the same, the energy goes down because of the long-range Coulombic attraction (dark gray). Thus, the two adiabatic curves (that nearly coincide with the two diabatic curves, especially for large R) are going to cross each other Figs. 6.16a–b but the two states have the same symmetry with respect to the molecular axis (as witnessed by $S \neq 0$) and, therefore, the crossing cannot occur, as shown in Fig. 6.16d. As a result, the two curves *avoid the crossing* and, as shown in Figs. 6.16c–f, the "atomic" curve switches to the "ionic" curve and vice versa. This switching means an electron jumping from Na to Cl and, therefore, formation of the ions Na^+ and Cl^- (then the ions approach fast - this is the *harpooning effect*, introduced to chemistry by Michael Polanyi). This jump occurs at long distances, of the order of 9 Å.

Is this jump inevitable?

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[70] It prevents the two cores collapsing; cf. Chapter 13.

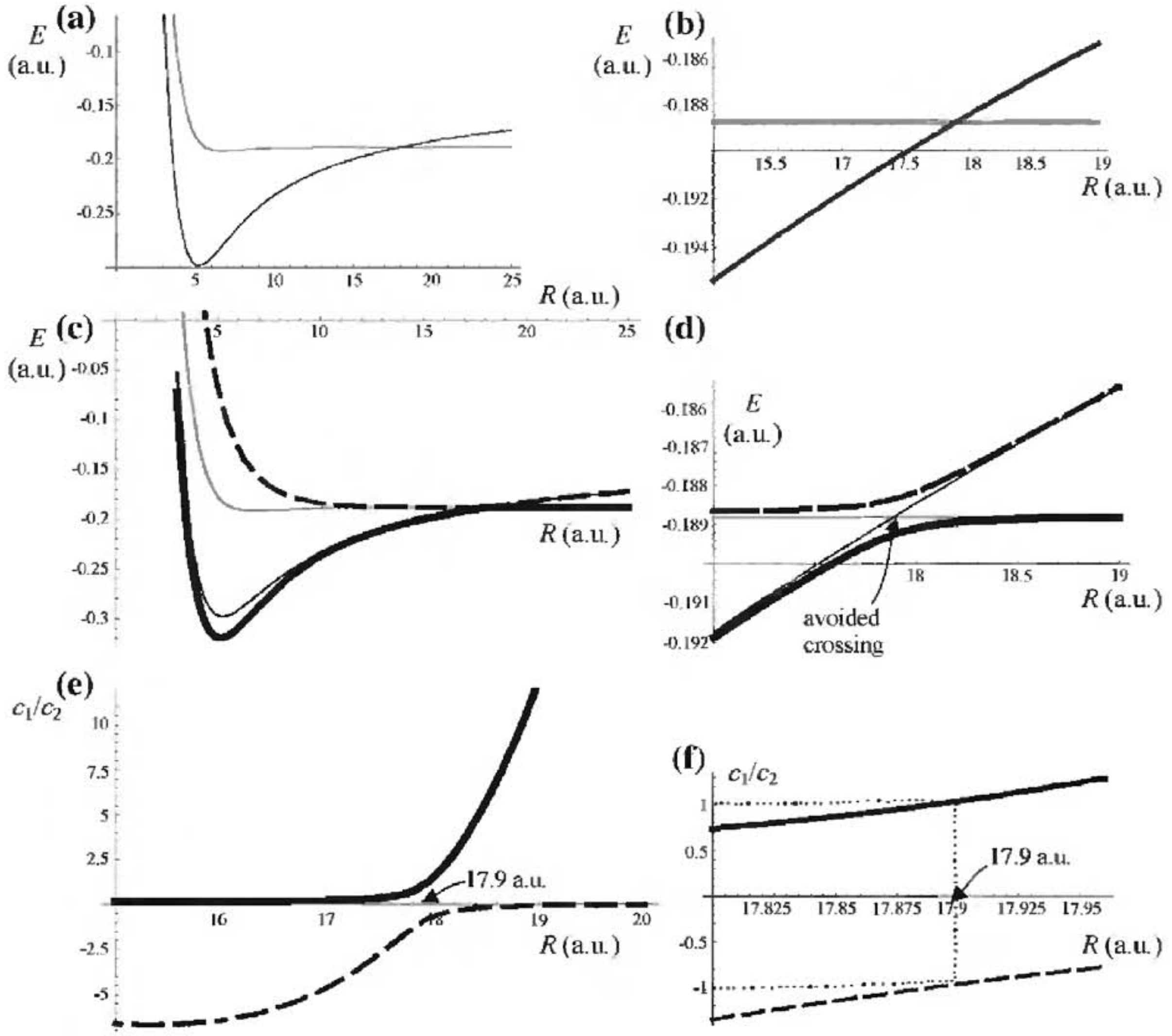

Fig. 6.16. A simple one-electron model of electron transfer in the NaCl molecule. (a) The mean values of the Hamiltonian with two *diabatic* states: one (light gray) being the 3*s* atomic orbital of the sodium atom (atomic curve), the second (dark gray) the $2p$ atomic orbital of the chlorine atom (ionic curve). The two diabatic curves intersect. (b) A closer view of the intersection. (c) The two diabatic curves [gray, as in (a,b)] and the two *adiabatic* curves (black), the lower-energy (solid), the higher-energy (dashed). Although the drawing looks like intersection, in fact the adiabatic curves "*repel*" each other, as shown in (d). (e) Each of the adiabatic states is a linear combination of two diabatic states (atomic and ionic). The ratio c_1/c_2 of the coefficients for the lower-energy (solid line) and higher-energy states (dashed line), c_1 is the contribution of the atomic function, c_2 – of the ionic function. As we can see, the lower-energy (higher-energy) adiabatic state is definitely atomic (ionic) for $R > 17.9$ a.u. and definitely ionic (atomic) for smaller R in the vicinity of the avoided crossing. (f) The ratio c_1/c_2 very close to the avoided crossing point. As we can see, at this point, one of the adiabatic states is the sum, and the other the difference of the two diabatic states.

If the electron is able to adapt instantaneously to the position of the nuclei (slow nuclear motion), the system follows the adiabatic curve. If the nuclear motion is very fast, the system follows the diabatic curve and no electron transfer takes place. The electron transfer is more probable if the gap $2|\mathcal{H}_{12}|$ between $E_+(R)$ and $E_-(R)$ is large.

In our model, for large distances, the adiabatic are practically identical with the diabatic states, except in the avoided crossing region (see Figs. 6.16c–d).

6.14 Polyatomic Molecules and Conical Intersection

Crossing for Polyatomics

The non-crossing rule for a diatomic molecule was based on Eq. (6.47). To achieve the crossing, we had to make vanish two independent terms with only one parameter (the internuclear distance R) to vary. It is important to note that in the case of a polyatomic molecule, the formula would be the same, but the number of parameters would be larger: $3M - 6$ in a molecule with M nuclei. For $M = 3$, therefore, one has already three such parameters. No doubt even for a three-atomic molecule, we would be able to make the two terms equal to zero and, therefore, achieve $E_+ = E_-$; i.e., the crossing of the two diabatic hypersurfaces would occur.

Let us investigate this possibility, which, for reasons that will become clear later, is called *conical intersection*. We will approach this concept by a few steps.

Cartesian System of 3M Coordinates ($\mathbf{O}_{3M}$)

All the quantities in Eq. (6.47) depend on $n = 3M - 6$ coordinates of the nuclei. These coordinates may be chosen in many different ways; the only thing we should bother about is that they have to determine the positions of M point objects. Just to begin, let us construct a Cartesian system of $3M$ coordinates ($\mathbf{O}_{3M}$). Let us locate (Fig. 6.17) nucleus 1 at the origin (in this way, we eliminate three degrees of freedom connected with the translation of the system), and nucleus 2 will occupy the point x_2 on the x-axis; i.e., $y_2 = z_2 = 0$. In this way, we have eliminated two rotations of the system. The total system may still be rotated about the x-axis.

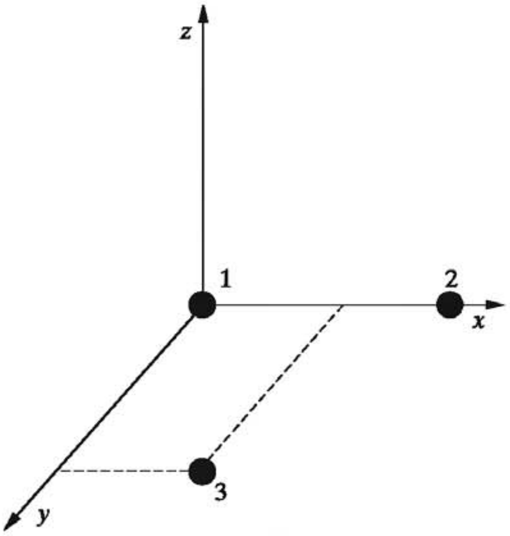

Fig. 6.17. The Cartesian coordinate system $\mathbf{O}_{3M}$ and the atoms 1, 2, and 3 with their fixed positions.

This last possibility can be eliminated when we decide to locate the nucleus 3 in the plane x, y (i.e., the coordinate $z_3 = 0$).

Thus, six degrees of freedom have been eliminated from the $3M$ coordinates. The other nuclei may be indicated by vectors (x_i, y_i, z_i) for $i = 4, 5, \ldots M$. As we can see, there has been a lot of arbitrariness in these choices.[71]

Cartesian System of 3M − 6 Coordinates ($\mathbf{O}_{3M-6}$)

This choice of coordinate system may be viewed a little differently. We may construct a Cartesian coordinate system with the origin at atom 1 and the axes x_2, x_3, and y_3 (see Fig. 6.17), and x_i, y_i, and z_i for $i = 4, 5, \ldots M$. Thus, we have a Cartesian coordinate system ($\mathbf{O}_{3M-6}$) with $3 + 3(M-3) = 3M - 6 = n$ axes, which may be labeled (in the sequence given above) in a uniform way: $\bar{x}_i, i = 1, 2, \ldots n$. A single point $\boldsymbol{R} = (\bar{x}_1, \bar{x}_2, \ldots \bar{x}_{3M-6})$ in this n-dimensional space determines the positions of all M nuclei of the system. If necessary, all these coordinates may be expressed by the old ones, but it will not be because our goal is different.

Two Special Vectors in the $\mathbf{O}_{3M-6}$ Space

Let us consider two functions $\bar{E}_1 - \bar{E}_2$ and V_{12} of the configuration of the nuclei $\boldsymbol{R} = (\bar{x}_1, \bar{x}_2, \ldots \bar{x}_{3M-6})$; i.e., with domain being the $\mathbf{O}_{3M-6}$ space. Now, let us construct two vectors in $\mathbf{O}_{3M-6}$:

$$\nabla(\bar{E}_1 - \bar{E}_2) = \sum_{i=1}^{3M-6} \boldsymbol{i}_i \left(\frac{\partial(\bar{E}_1 - \bar{E}_2)}{\partial \bar{x}_i}\right)_0,$$

$$\nabla V_{12} = \sum_{i=1}^{3M-6} \boldsymbol{i}_i \left(\frac{\partial V_{12}}{\partial \bar{x}_i}\right)_0,$$

where $\boldsymbol{i}_i$ stands for the unit vector along axis $\bar{x}_i$, while the derivatives are calculated in a point of the configurational space for which

$$\sqrt{\left(\frac{\bar{E}_1 - \bar{E}_2}{2}\right)^2 + |V_{12}|^2} = 0;$$

i.e., where according to Eq. (6.47), one has the intersection of the adiabatic hypersurfaces.

6.14.1 Branching Space and Seam Space

We may introduce any coordinate system. We are free to do this because our object (molecule) stays immobile, but our way of determining the nuclear coordinates changes. We will change

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[71] By the way, if the molecule were diatomic, the third rotation need not be determined and the number of variables would be equal to $n = 3 \times 2 - 5 = 1$.

the coordinate system in n-dimensional space once more. This new coordinate system is formed from the old one ($\mathbf{O}_{3M-6}$) by rotation.

> The rotation will be done in such a way as to make the plane determined by the two first axes ($\bar{x}_1$ i $\bar{x}_2$) of the old coordinate system coincide with the plane determined by the two vectors: $\nabla(\bar{E}_1 - \bar{E}_2)$ oraz $\nabla(V_{12})$,

Let us denote the coordinates in the rotated coordinate system by ξ_i, $i = 1, 2, \ldots, n$. The new coordinates can, of course, be expressed as some linear combinations of the old ones, but these details need not concern us. The most important thing is that we have the axes of the coordinates ξ_1 and ξ_2, which determine the same plane as the vectors $\nabla\left(\bar{E}_1 - \bar{E}_2\right)$ and ∇V_{12}. This plane is known as the *branching space (plane)*. The space of all vectors $\left(0.0, \xi_3 \ldots \xi_{3M-6}\right)$ is called the *seam space*. The directions $\nabla\left(\bar{E}_1 - \bar{E}_2\right)$ and ∇V_{12} need not be orthogonal, although they look this way in illustrations shown in the literature.[72]

Now we are all set to define the conical intersection.

6.14.2 Conical Intersection

Why has this slightly weird coordinate system been chosen? We see from the formula [Eq. (6.47)] for E_+ and E_- that ξ_1 and ξ_2 correspond to the fastest change of the first term and the second term under the square-root sign, respectively.[73]

> Any change of other coordinates (along the axes orthogonal to the plane $\xi_1\xi_2$) does not influence the value of the square root; i.e., it does not change the difference between E_+ and E_- (although the values of E_+ and E_- change).

Therefore, the hypersurface E_+ intersects with the hypersurface E_-, and their common part (i.e., the seam space) are all those vectors of the n-dimensional space that fulfill the condition: $\xi_1 = 0$ and $\xi_2 = 0$. The intersection represents a $(n-2)$−dimensional subspace of the n-dimensional space of the nuclear configurations.[74] When we withdraw from the point

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[72] See F. Bernardi, M. Olivucci, and M.A. Robb, *Chem. Soc. Rev., 25*, 321 (1996). The authors confirmed to me that the angle between these vectors is often quite small.

[73] Let us take a scalar field V and calculate its value at the point $\boldsymbol{r}_0 + \boldsymbol{r}$, where we assume $|\boldsymbol{r}| \ll 1$. From the Taylor expansion, we have with good accuracy, $V\left(\boldsymbol{r}_0 + \boldsymbol{r}\right) = V(\boldsymbol{r}_0) + \left(\nabla V\right)_{\boldsymbol{r}=\boldsymbol{r}_0} \cdot \boldsymbol{r} = V(\boldsymbol{r}_0) + \left|\left(\nabla V\right)_{\boldsymbol{r}=\boldsymbol{r}_0}\right| \cdot r\cos\theta$. We obtain the largest absolute value of the increment of V for $\theta = 0$ and $\theta = 180°$ i.e., along the vector $\left(\nabla V\right)_{\boldsymbol{r}=\boldsymbol{r}_0}$.

[74] If the axes ξ_1 and ξ_2 were chosen in another way on the plane determined by the vectors $\nabla\left(\bar{E}_1 - \bar{E}_2\right)$ and ∇V_{12}, the conical intersection would be described in a similar simple way. If, however, the axes were chosen outside the plane, it may happen that moving along more than just two axes, they would split into E_+ and E_-. Our choice stresses that the intersection of E_+ and E_- represents a $(n-2)$ − dimensional subspace (seam space).

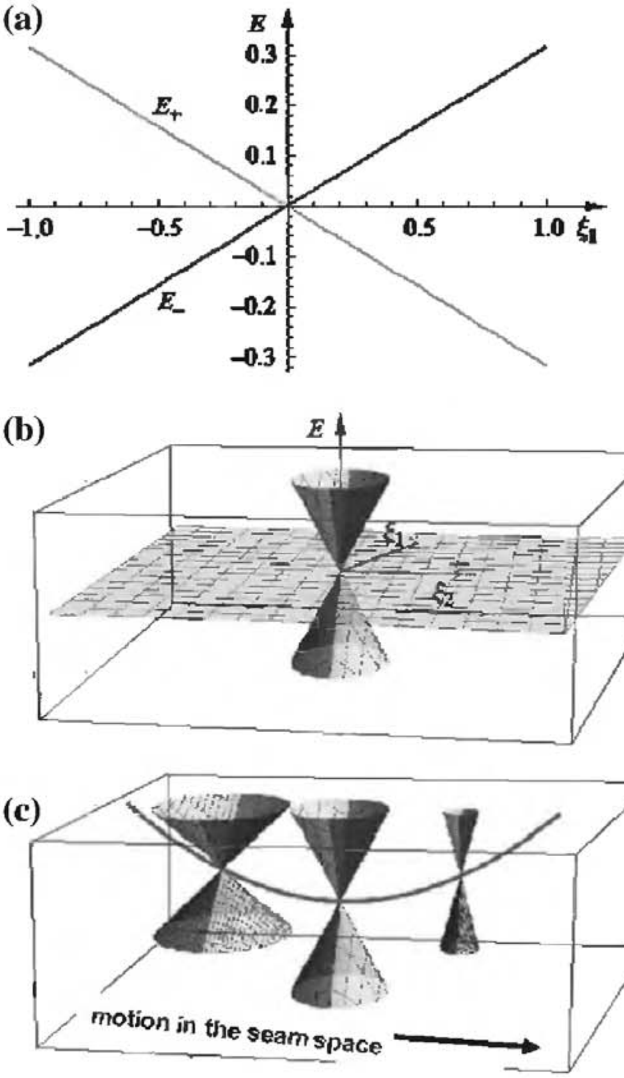

Fig. 6.18. Conical intersection (scheme). E represents the electronic energy as a function of coordinates of the nuclei: $\xi_1, \xi_2, \xi_3, \xi_4, \ldots \xi_{3M-6}$. This shows only the coordinates ξ_1 and ξ_2, which define what is known as the *branching space* $\xi_1 \xi_2$, while the space of all vectors $(0, 0, \xi_3, \xi_4, \ldots \xi_{3M-6})$ known as the seam space is not shown in panel (a) or (b). (a) Section of the cones along ξ_1 at a given point of the seam space; the equality $E_+ = E_-$ holds for the conical intersection point. (b) The vectors $\nabla(\bar{E}_1 - \bar{E}_2)$ and ∇V_{12} span the branching plane (the horizontal plane; both vectors are calculated at the conical intersection). The upper cone E_+ and the lower cone E_- correspond to Eq. (6.47), and each consists of two diabatic surfaces (gray and white). (c) Staying at the branching point $(0, 0)$, but moving in the seam space, one remains all the time in the conical intersection, but the cones look different (different cone openings) and the energy $E_+ = E_-$ changes (solid line).

$(0, 0, \xi_3, \xi_4, \ldots \xi_{3M-6})$ by changing the coordinates ξ_1 and/or ξ_2, a difference between E_+ and E_- appears. For small increments $d\xi_1$, the changes in the energies E_+ and E_- are proportional to $d\xi_1$ and for E_+ and E_- differ in sign. This means that the hypersurfaces E_+ and E_- as functions of ξ_1 (at $\xi_2 = 0$ and fixed other coordinates) have the shapes shown in Fig. 6.18a. For ξ_2, the situation is similar, but the cone may differ by its angle. From this, it follows that the ground and excited state hypersurfaces intersect with each other (the intersection set represents the subspace of all vectors $(0, 0, \xi_3, \xi_4, \ldots, \xi_n)$) and split when we go out of the intersection point according to the *cone rule*; i.e., E_+ and E_- change *linearly* when moving in the plane ξ_1, ξ_2 from the point $(0, 0)$.

This is called the *conical intersection* (see Fig. 6.18b). The cone opening angle is in general different for different points of the seam space (see Fig. 6.18c).

The conical intersection plays a fundamental role in the theory of chemical reactions (Chapter 14). The lower (ground-state) as well as the higher (excited-state) hypersurfaces are composed of two diabatic parts, which in polyatomics correspond to different patterns of chemical bonds. This means that the system (represented by a point) when moving on the ground-state adiabatic hypersurface toward the join of the two parts, passes near the conical intersection point, over the energy barrier, and goes to the products. This is the essence of a chemical reaction.

6.14.3 Berry Phase

We will focus on the adiabatic wave functions close to the conical intersection. Our goal will be to show something strange, that

when going around the conical intersection point in the configurational space, the electronic wave function changes its phase; and after coming back to the starting point, this change results in the opposite sign of the function.

First, let us prepare an itinerary in the configuration space around the conical intersection. We need a parameter, which will be an angle α and will define our position during our trip around the point. Let us introduce some abbreviations in Eq. (6.47): $\Delta \equiv \frac{\bar{E}_1-\bar{E}_2}{2}$, $h \equiv V_{12}$, and define α in the following way:

$$\sin\alpha = \Delta/\rho,$$

$$\cos\alpha = h/\rho,$$

$$\text{where } \rho = \sqrt{\Delta^2 + h^2}.$$

We will move around the conical intersection within the plane given by the vectors $\nabla\Delta$ and ∇h (branching plane). The conical intersection point is defined by $|\nabla\Delta| = |\nabla h| = 0$. Changing α from 0 to 2π, we have to go, at a distance $\rho(\alpha)$, once through a maximum of h (say, in the direction of the maximum gradient ∇h), and once through its minimum $-h$ (the opposite direction). This is ensured by $\cos\alpha = h/\rho$. Similarly, we have a single maximum and a single minimum of $\nabla\Delta$ (as must happen when going around), when assuming that $\sin\alpha = \Delta/\rho$. We do not need more information about our itinerary because we are interested in how the wave function changes after making a complete trip (i.e., 360° around the conical intersection and returning to the starting point).

The adiabatic energies are given in Eq. (6.47) and the corresponding coefficients of the diabatic states are reported in Appendix D available at booksite.elsevier.com/978-0-444-59436-5 (the first, most general case):

$$\left(\frac{c_1}{c_2}\right)_{\pm} = \frac{1}{h}\left[\Delta \pm \sqrt{\Delta^2 + h^2}\right] = \tan\alpha \pm \frac{1}{\cos\alpha}.$$

Thus,

$$\frac{c_{1,+}}{c_{2,+}} = \frac{\sin\alpha + 1}{\cos\alpha} = \frac{\left(\sin\frac{\alpha}{2} + \cos\frac{\alpha}{2}\right)^2}{\cos^2\frac{\alpha}{2} - \sin^2\frac{\alpha}{2}} = \frac{\left(\sin\frac{\alpha}{2} + \cos\frac{\alpha}{2}\right)}{\left(\cos\frac{\alpha}{2} - \sin\frac{\alpha}{2}\right)},$$

$$\frac{c_{1,-}}{c_{2,-}} = \frac{\sin\alpha - 1}{\cos\alpha} = \frac{-\left(\cos\frac{\alpha}{2} - \sin\frac{\alpha}{2}\right)^2}{\cos^2\frac{\alpha}{2} - \sin^2\frac{\alpha}{2}} = -\frac{\left(\cos\frac{\alpha}{2} - \sin\frac{\alpha}{2}\right)}{\left(\cos\frac{\alpha}{2} + \sin\frac{\alpha}{2}\right)}.$$

To specify the coefficients in $\psi_+ = c_{1,+}\psi_1 + c_{2,+}\psi_2$ and $\psi_- = c_{1,-}\psi_1 + c_{2,-}\psi_2$, with ψ_1 and ψ_2 denoting the diabatic states, we have to take the two normalization conditions into account: $c_{1,+}^2 + c_{2,+}^2 = 1$, $c_{1,-}^2 + c_{2,-}^2 = 1$ and the orthogonality of ψ_+ and ψ_- : $c_{1,+}c_{1,-} + c_{2,+}c_{2,-} = 0$. After a little algebra, we get

$$c_{1,+} = \frac{1}{\sqrt{2}}\left(\cos\frac{\alpha}{2} + \sin\frac{\alpha}{2}\right),$$

$$c_{2,+} = \frac{1}{\sqrt{2}}\left(\cos\frac{\alpha}{2} - \sin\frac{\alpha}{2}\right).$$

$$c_{1,-} = -\frac{1}{\sqrt{2}}\left(\cos\frac{\alpha}{2} - \sin\frac{\alpha}{2}\right),$$

$$c_{2,-} = \frac{1}{\sqrt{2}}\left(\cos\frac{\alpha}{2} + \sin\frac{\alpha}{2}\right).$$

Now, let us consider the wave functions ψ_+ and ψ_- at the angle α and at the angle $\alpha + 2\pi$. Note that $\cos\frac{\alpha+2\pi}{2} = \cos\left(\frac{\alpha}{2} + \pi\right) = -\cos\frac{\alpha}{2}$ and $\sin\frac{\alpha+2\pi}{2} = \sin\left(\frac{\alpha}{2} + \pi\right) = -\sin\frac{\alpha}{2}$. Therefore, both the electronic functions ψ_+ and ψ_- have to change their signs after the journey (i.e., the "*geometric*" phase or Berry phase); that is,

$$\psi_+(\alpha + 2\pi) = -\psi_+(\alpha)$$

and

$$\psi_-(\alpha + 2\pi) = -\psi_-(\alpha).$$

This is how the conical intersection is usually detected.

Since the total wave function has to be single-valued, this means the function that describes the motion of the nuclei (and multiplies the electronic function) has to compensate for that change and also undergo a change of sign.

The Berry phase has some interesting analogy to gymnastics; (see p. 902).

The Role of the Conical Intersection–Non-radiative Transitions and Photochemical Reactions

The conical intersection was underestimated for a long time. However, photochemistry demonstrated that it happens much more frequently than expected. Laser light may excite a molecule from its ground state to an excited electronic state (Fig. 6.19).

Let us assume that the nuclei in the electronic ground state have their optimal positions characterized by point 1 in the configurational space (they vibrate in its neighborhood but let us ignore the quantum nature of these vibrations[75]).

The change of electronic state takes place so fast that the nuclei do not have enough time to move. Thus the positions of the nuclei in the excited state are identical to those in the ground state (Franck-Condon rule).

Point 2 (FC) in Fig. 6.19 shows the very essence of the Franck-Condon rule–a vertical transition. The corresponding nuclear configuration may differ quite significantly from the nearest potential energy minimum (point 3) in the excited-state PES. In a few femtoseconds, the system slides down from FC to the neighborhood of point 3, transforming its potential energy into kinetic energy. Usually point 3 is separated from the conical intersection configuration 5 by a barrier with the corresponding potential energy saddle point 4 ("*transition state*"). Behind the saddle point, there is usually an energy valley[76] with a deep funnel ending in the conical intersection configuration (point 5). As soon as the system overcomes the barrier at the transition state (4), by going over it or by tunneling, it will be sucked in by the conical intersection attractor with almost 100% probability.

The system goes through the "*funnel*" to the electronic ground-state hypersurface with probability 1.

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[75] Electronic energy hypersurfaces represent the PES for the motion of the nuclei. In the quantum mechanical picture, only some energies will be allowed: we will have the vibrational and rotational energy levels, as for diatomics. The same energy levels corresponding to E_+ may be close in the energy scale to those of E_-. Moreover, it may happen that the vibrational wave functions of two such levels may overlap significantly in space, which means that there is a significant probability that the system will undergo a transition from one to the other vibrational state. In short, in the quantum mechanical picture, the motion of the system is not necessarily bound to a single PES, but the two PESs are quite penetrable.

[76] This is on the excited-state PES.

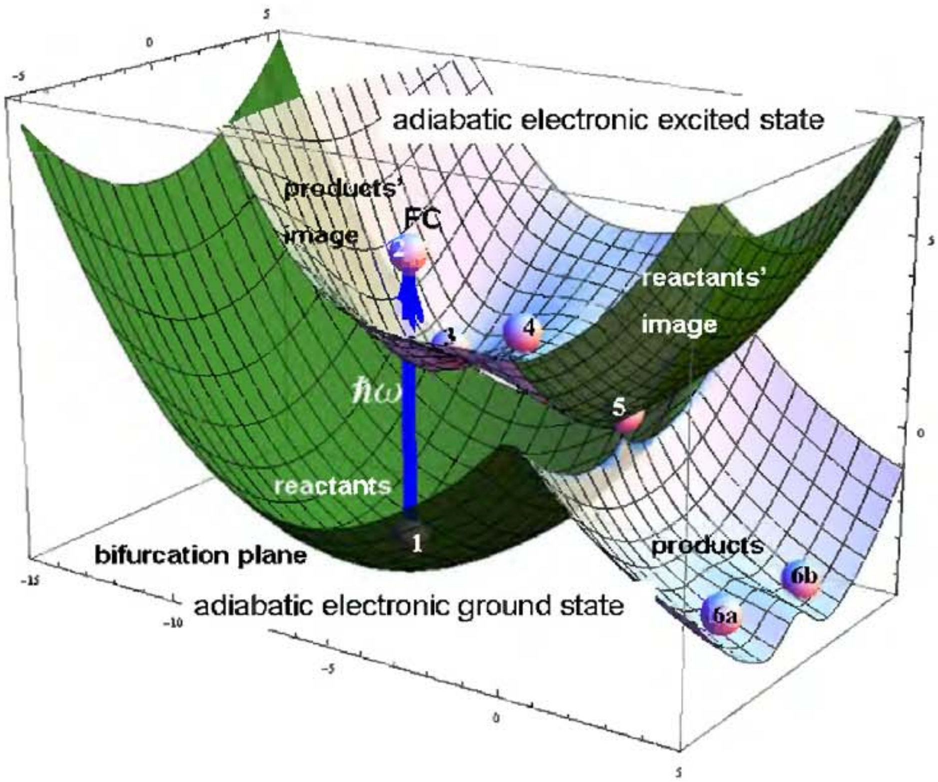

Fig. 6.19. Non-radiative transitions explained by the photochemical funnel effect (related to the conical intersection). This shows the electronic energy as a function of the coordinates ξ_1 and ξ_2 within the branching space. a) There are two adiabatic surfaces: the lower one corresponds to the ground electronic state (E_-), and the upper one pertains the excited electronic state (E_+). Each of the surfaces is composed of two parts corresponding originally to the diabatic states: the darker one corresponds to the electronic structure of the reactants, the lighter one corresponds to the electronic structure of the products. The spheres indicate some particular configuration of the nuclei. Sphere 1 indicates the reactants, and the arrow symbolizes a photoexcitation by absorption of a photon with the appropriate energy $h\nu = \hbar\omega$. The excitation takes place instantaneously at a fixed reactants' configuration (Franck-Condon rule), but the electronic excited state corresponds already to the products, and the forces acting on the nuclei correspond to the excited surface slope at the point labeled FC (sphere 2). The forces make the system move towards the minimum (sphere 3). If the kinetic energy acquired is large enough to overcome the barrier (sphere 4), the system enters the funnel, inevitably reaches the conical intersection point (sphere 5), and in a radiationless process, begins moving on the ground-state adiabatic hypersurface. The system may end up at different products (spheres 6a and 6b), or it may go back to the configuration of the reactants (sphere 1).

Then the system will continue its path in the ground-state PES, E_-, going either toward products $6a$ or $6b$, or going back to point 1 (non-reactive path).

Of course, the total energy has to be conserved. The non-radiative process described will take place if the system finds a way to dissipate its energy; i.e., to transfer an excess of electronic energy into the vibrational, rotational, and translational degrees of freedom of its own or neighboring molecules (e.g., of the solvent).[77]

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[77] The energy is usually distributed among the degrees of freedom in an unequal way.

We may ask whether we will find some other conical intersections in the ground-state PES. In general, the answer is positive. There are at least two reasons for this.

> In the simplest case, the conical intersection represents the dilemma of an atom C (approaching molecule AB): attach to A or attach to B?

Thus, any encounter of three atoms causes a conical intersection (we will come back to this in Chapter 14). In *each* case, the important thing is a configuration of nuclei, where a small variation may lead to distinct sets of chemical bonds. Similar "pivot points" may happen for four, five, six, or more atoms. Thus, we will encounter not only the minima, maxima, and saddle points, but also the conical intersection points when traveling in the ground-state PES.

The second reason is the permutational symmetry. Very often, the system contains the same kinds of nuclei. Any exchange of the positions of such nuclei moves the point representing the system in configuration space to some distant regions, whereas the energy does not change at all. Therefore, any PES has to exhibit the corresponding permutational symmetry. All the details of PES will repeat $M!$ times for a system with M identical nuclei. This will multiply the number of conical intersections.

More information about conical intersection will be given in Chapter 14, when we will be equipped with the theoretical tools to describe how the electronic structure changes during chemical reactions.

6.15 Beyond the Adiabatic Approximation

6.15.1 Vibronic Coupling

In polyatomic molecules, a diabatic state represents a product of an electronic wave function $\psi_i^{(\Gamma_1)}$ and a rovibrational function[78] $f_v^{(\Gamma_2)}$; i.e., a *rovibronic state*:

$$\psi_i^{(\Gamma_1)}\left(\boldsymbol{r};\boldsymbol{R}\right) f_v^{(\Gamma_2)}(\boldsymbol{R}), \tag{6.51}$$

where the upper indices are related to the irreducible representations of the symmetry group of the clamped-nuclei Hamiltonian that the functions belong to (i.e., according to which the corresponding functions transform; see Appendix C available at booksite.elsevier.com/978-0-444-59436-5, p. e17). If one considers the electronic and the vibrational states only[79] Eq. (6.51) denotes a *vibronic state*. The product function transforms according to the direct product representation $\Gamma_1 \times \Gamma_2$.

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[78] This function describes rotations and vibrations of the molecule.

[79] For the sake of simplicity, we are skipping the rotational wave function.

If one is interested in those solutions of the Schrödinger equation, which belong to the irreducible representation Γ, the function $\psi_i^{(\Gamma_1)}(\boldsymbol{r};\boldsymbol{R})f_v^{(\Gamma_2)}(\boldsymbol{R})$ is useful as a basis function only if $\Gamma_1 \times \Gamma_2$ contains Γ. For the same reason, another basis function may be useful $\psi_{i'}^{(\Gamma_3)}(\boldsymbol{r};\boldsymbol{R})f_{v'}^{(\Gamma_4)}(\boldsymbol{R})$, as well as other similar functions:

$$\psi^{(\Gamma)} = c_{i1}\psi_i^{(\Gamma_1)}\left(\boldsymbol{r};\boldsymbol{R}\right) f_1^{(\Gamma_2)}(\boldsymbol{R}) + c_{i'2}\psi_{i'}^{(\Gamma_3)}\left(\boldsymbol{r};\boldsymbol{R}\right) f_2^{(\Gamma_4)}(\boldsymbol{R}) + \cdots \tag{6.52}$$

If, say, coefficients c_{i1} and $c_{i'2}$ are large, an effective superposition of the two vibronic states is taking place, which is known as *vibronic coupling*.

We are, therefore, beyond the adiabatic approximation (which requires a single vibronic state, a product function) and the very notion of the single potential energy hypersurface for the motion of the nuclei becomes irrelevant. In the adiabatic approximation, the electronic wave function is computed from Eq. (6.8) with the clamped nuclei Hamiltonian; i.e., the electronic wave function does not depend on what the nuclei are *doing*, but only where they *are*. In other words, the electronic structure is determined [by finding a suitable $\psi_i^{(\Gamma_1)}(\boldsymbol{r};\boldsymbol{R})$ through solution of the Schrödinger equation] at fixed position $\boldsymbol{R}$ of the nuclei. This implies that in this approximation, the electrons always have enough time to adjust themselves to any instantaneous position of the nuclei. One may say that in a sense, the electrons and the nuclei are perfectly correlated in their motion: electrons follow the nuclei. Therefore,

a non-adiabatic behavior (or vibronic coupling) means a weakening of this perfect correlation, which is equivalent to saying that it may happen that the electrons do not have enough time to follow a (too-fast) motion of the nuclei.

This weakening is usually allowed by taking a linear combination of Eq. (6.52), which may be thought as a kind of frustration for electrons which vibration ("type of motion") of the nuclei to follow. If $\Gamma_1 \neq \Gamma_3$ and $\Gamma_2 \neq \Gamma_4$, one may say that we have to do with such an electronic state, which resembles $\psi_i^{(\Gamma_1)}$, when the molecule participates in a vibration of symmetry Γ_2 and resembles $\psi_{i'}^{(\Gamma_3)}$, when the molecule vibrates according to Γ_4.

This idea may be illustrated by the following examples.

Example 1: Dipole-Bound Electron

Imagine a molecular dipole. One may think of it as having a + and a − pole. We are interested in its + pole, because now we consider an extra electron, which will be bound with the dipole by the + pole-electron attraction. Obviously, such an attraction should depend on the dipole

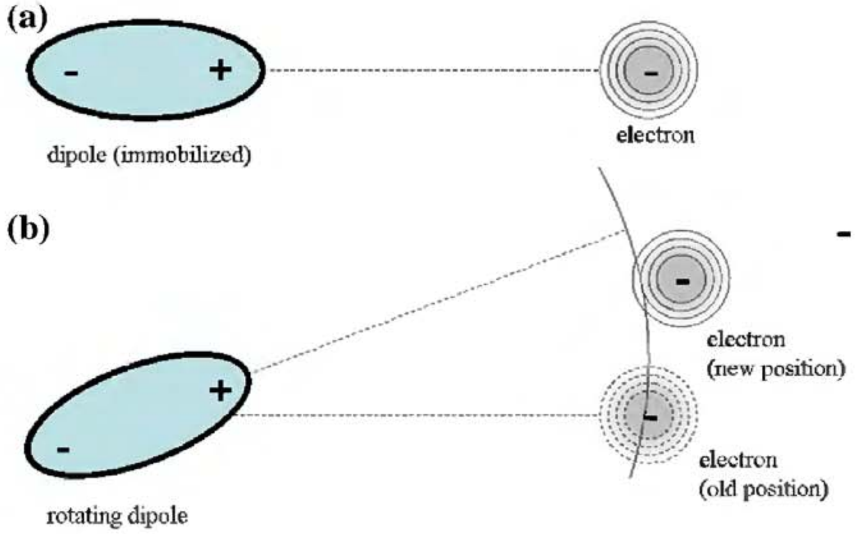

Fig. 6.20. A strange situation: An electron is unable to follow the motion of the nuclei (we are beyond the adiabatic approximation, a non-adiabatic case). (a) Some molecular dipoles with a sufficiently large dipole moment may bind an extra electron (a cloud on the right), which in such a case is far from the dipole and is attracted by its pole. The positive pole plays a role of a pseudonucleus for the extra electron. (b) When the dipole starts to rotate (a state with a nonzero angular momentum), the electron follows the motion of the pole. This is, however, difficult for high angular momenta (the electron has not enough time to adapt its position right toward the pole), and it is even harder because the centrifugal force pushes the extra electron farther away.

moment of the dipolar molecule. How strong must a point dipole be to be able to bind an electron? This question has been already asked, and the answer[80] is that this happens for the pointlike dipole moment larger than[81] 1.625 D. If the dipole itself represents an electronic closed shell molecule, the extra electron is usually very far (see Fig. 6.20a), even at distances of the order of 50 Å.

Now imagine the dipole starts to rotate (see Fig. 6.20b). At small angular momentum, the electron supposedly does not have any problem with following the motion of the positive pole. For larger angular momenta, the electron speeds up, its distance to the dipole increases due to the centrifugal force, and when this happens, it gets harder and harder to follow the motion of the positive pole. The electron does not have enough time. This means a larger and larger non-adiabatic correction.

Example 2: Hydrogen Molecule

Let us form two diabatic states: $\psi_i^{(\Gamma_1)}(\boldsymbol{r}; R)$ corresponding to the double occupation of the bonding orbital $1s_a + 1s_b$ and the other, $\psi_{i'}^{(\Gamma_3)}(\boldsymbol{r}; R)$, corresponding to the double occupation of the bonding excited orbital $2s_a + 2s_b$. In this case, we will take $\Gamma_3 = \Gamma_1$ (it does not mean

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[80] E. Fermi and E. Teller, *Phys. Rev.*, *47*, 399 (1947).

[81] For non-pointlike dipoles, one may expect this limiting value to be less important, since the essence of the problem is binding an electron by a positive charge. This, however, happens even for marginally small positive charges (see the hydrogen-like atom).

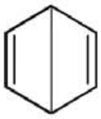
the f functions are the same). The rovibrational function will be taken as (we assume the vibrational and rotational ground state) $f_1^{(\Gamma_2)}(\boldsymbol{R}) = \chi_1(R)Y_0^0(\theta,\phi) = \chi_1(R)$, but $f_2^{(\Gamma_4)}(\boldsymbol{R}) = \chi_2(R)Y_0^0(\theta,\phi) = \chi_2(R)$. The vibrational ground state $\chi_1(R)$ has its maximum at $R = R_{1s}$, where the minimum of the potential energy curve $E_{1s}(R)$ is, while $\chi_2(R)$ has its maximum at $R = R_{2s} > R_{1s}$, where the potential energy curve $E_{2s}(R)$ exhibits the minimum. The mixing coefficients c_{i1} and c_{i2} will obviously depend on R. For $R = R_{1s}$, we will have $c_{i1} \gg c_{i2}$, because the ground-state bonding orbital will describe well the electronic charge distribution, and for this R, the $2s_a+2s_b$ orbital will have a very high energy (the size of the $2s$ orbitals does not fit the distance). However, when R increases, the energy corresponding to $1s_a+1s_b$ will increase, while the energy corresponding $2s_a + 2s_b$ will decrease (because of better fitting). This will result in a more important value of $|c_{i2}|$ and a bit smaller value of $|c_{i1}|$ than it was for $R = R_{1s}$. There is, therefore, a coupling of vibration with the electronic state–a vibronic coupling.

Example 3: Harpooning Effect

The harpooning effect from p. 308 represents also an example of a vibronic coupling, if the two diabatic states: the ionic one $\psi_i^{(\Gamma_1)}(\boldsymbol{r}; R)$ and the neutral one $\psi_{i'}^{(\Gamma_3)}(\boldsymbol{r}; R)$ are considered with their corresponding vibrational states.

Example 4: Benzene

Let us take a benzene molecule. Chemists have realized for a long time that all CC bonds in this molecule are equivalent (some quantum chemical arguments for this view were presented on p. 167). The benzene molecule does not represent a static hexagonal object. The molecule undergoes $3M - 6 = 30$ vibrations (normal modes, which will be discussed in Chapter 7). One of these modes, say, described by the vibrational wave function $f_v^{(\Gamma_2)}(\boldsymbol{R})$, resembles a kind of ring pulsing ("*breathing*"), and during these vibrations, the electronic wave function $\psi_i^{(\Gamma_1)}(\boldsymbol{r}; \boldsymbol{R})$ describes the six equivalent CC bonds. There is also another vibrational mode corresponding the vibrational function $f_{v'}^{(\Gamma_4)}(\boldsymbol{R})$, that, in its certain phase, corresponds to shortening of the two opposite CC bonds and lengthening of the four other CC bonds. During such a motion, the electronic structure changes and will correspond to what is known as the *Dewar structure*:



(the shortened bonds will resemble double bonds, and the others will resemble single bonds), corresponding to the electronic wave function $\psi_{i'}^{(\Gamma_3)}(\boldsymbol{r}; \boldsymbol{R})$. There will be much more such possibilities what is symbolized in Eq. (6.52) by "...".

The rovibrational functions $f_v^{(\Gamma_2)}(\boldsymbol{R})$ and $f_{v'}^{(\Gamma_4)}(\boldsymbol{R})$ must exhibit a strong asymmetry with respect to the equilibrium point (*vibronic anharmonicity*). Indeed, it is natural that the abovementioned Dewar structure is energetically favored for the vibrational deviations that shorten the to-be-double CC bond and becomes unfavorable for the opposite deviations.

6.15.2 Consequences for the Quest of Superconductors

Superconductivity, discovered by a Dutch scholar Heike Kammerlingh Onnes in 1911, is certainly a fascinating phenomenon. In some substances (like originally in mercury, tin, and lead), measurement of the electric conductivity as a function of lowering the temperature ended up by an abrupt decrease (below a critical temperature) of the electric resistance to zero value. Such a property would be great for operating technical devices or sending electric energy at large distances. The problem is that the critical temperature turned out to be extremely low–until 1987, it was always lower than about 23 K. The situation changed after discovery of what is now known as high-temperature superconductors (HTS) by J. George Bednorz and K. Alex Müller in 1987. Nowadays, after discovering hundreds of new HTSs, the highest critical temperature found is equal to about 164 K. In virtually all cases, it turned out that the HTSs have a characteristic atomic layer structure with alternating copper and oxygen atoms.

The "Magic" Cu–O Distance

No current theory explains properly the phenomena exhibited by HTSs. There are several theoretical concepts, but their striking weakness is that they provide no indication as to the class of promising materials that one should look for the HTS. After decades of research, an intriguing conclusion has been however found, that the closer the Cu–O distance to a "*magic value*" $R_{Cu-O} = 1.922$ Å is, the higher the corresponding critical temperature is.[82] This remarkable correlation went virtually unnoticed by the solid-state physics community for a long time.

How could such a precise criterion work? Well, this strongly suggests that something important happens at distance $R_{Cu-O} = 1.922$ Å, but for some reason, it does not when it is away from this value.

Primum non Nocere...[83]

Why does a bulb emit light? It happens because the motion of the electrons in a thin wire inside the bulb meets a resistance of chaotic vibrations of the nuclei. The kinetic energy of the electrons (resulting from the electric power plant operation for our money) goes partially for making collisions with the nuclei. These collisions lead to high-energy electronic states, which emit light when relaxing. In principle, this is why we pay our electric bill.

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[82] C.N.R. Rao and A.K. Ganguli, *Chem. Soc. Review*, *24*, 1 (1995).

[83] "*First, do no harm*"–a phrase attributed to Greek physician Hippocrates (460–370 B.C.) as a suggested minimum standard for medical doctors.

And what if the nuclear motion, instead of interfering, helped electrons to move? Well, then the resistance would drop, just similarly as it does in superconductivity. Maybe there is something in it.

In 1993, Jeremy K. Burdett postulated some possible reason for superconductivity.[84] His hypothesis is related to a crossing of potential energy curves, precisely the subject of our earlier interest. According to Burdett, the "*magic Cu–O distance*" possibly corresponds to a crossing of two close-in-energy electronic diabatic states: a diabatic state characterized by the electron holes mainly on the copper atoms and another one with the electron holes mainly on the oxygen atoms. Thus, these two states differ by the electronic charge distribution[85], similarly as it was in NaCl (see p. 308). However, unlike as it was for NaCl, the minima, according to Burdett, do not differ much (if at all) in energy. Another important difference is that for NaCl, the crossing takes place for the Na-Cl distances that are several times larger than the nearest neighbor Na-Cl distance in the crystal of the rock salt, while for the HTSs, the Cu-O distance in crystals is close to the corresponding crossing point. This means that atomic vibrations may cause oscillating about the crossing point. As usually, from crossing of the diabatic curves, two adiabatic states appear: the ground state with the double minimum and an excited state (see Fig. 6.21).

Burdett's main point is the coupling of the ground vibrational state with the two diabatic electronic states. It is during such vibrations that a dramatic change of the electronic charge distribution is supposed to take place (strong *vibronic coupling*). The position of the vibrational level on the energy scale is said to be critical for superconductivity. If the position is substantially lower than the energy of the top of the barrier (Fig. 6.21b), one has to do with either of the two states localized in a given well. This corresponds to no communication between the wells, and we have to deal with either of the two different charge distributions (a "*mixed-valence*" compound). If, on the other hand, the vibrational level has large energy (Fig. 6.21c), high above the barrier top energy, one receives an averaged charge distribution, which does not change much during vibrations. According to Burdett, the superconductivity appears, when the vibrational level is close to the same energy as that of the top of the barrier (Fig. 6.21d), this causes a strong coupling of the two diabatic electronic states through the vibrational state.

Relevant Vibrations

It is natural to imagine that the electron transfer between two atoms (of type A) may be accomplished by a mediator–a third object, say atom B. This is why research began from studies of the effectivity of the transfer of an extra electron in the ABA^- system, like Na^+ F^- Na^0 (i.e., $A \equiv Na^+$, $A^- \equiv Na^0$, $B \equiv F^-$), when B oscillates between atoms A. Therefore, the

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[84] J.K. Burdett, *Inorg. Chem.*, *32*, 3915 (1993).

[85] Most probably, the key phenomena take place in the copper-oxygen layers and may be described as a reversible reaction $Cu^{3+} + O^{2-} \rightleftharpoons Cu^{2+\cdot} + O^{-\cdot}$ or $Cu^{2+\cdot} + O^{2-} \rightleftharpoons Cu^{+} + O^{-\cdot}$ (a dot means an unpaired electron). The presence of the unpaired electrons implies some ferro- or/and antiferromagnetic properties of these materials, which indeed have been discovered in the HTS phenomenon.

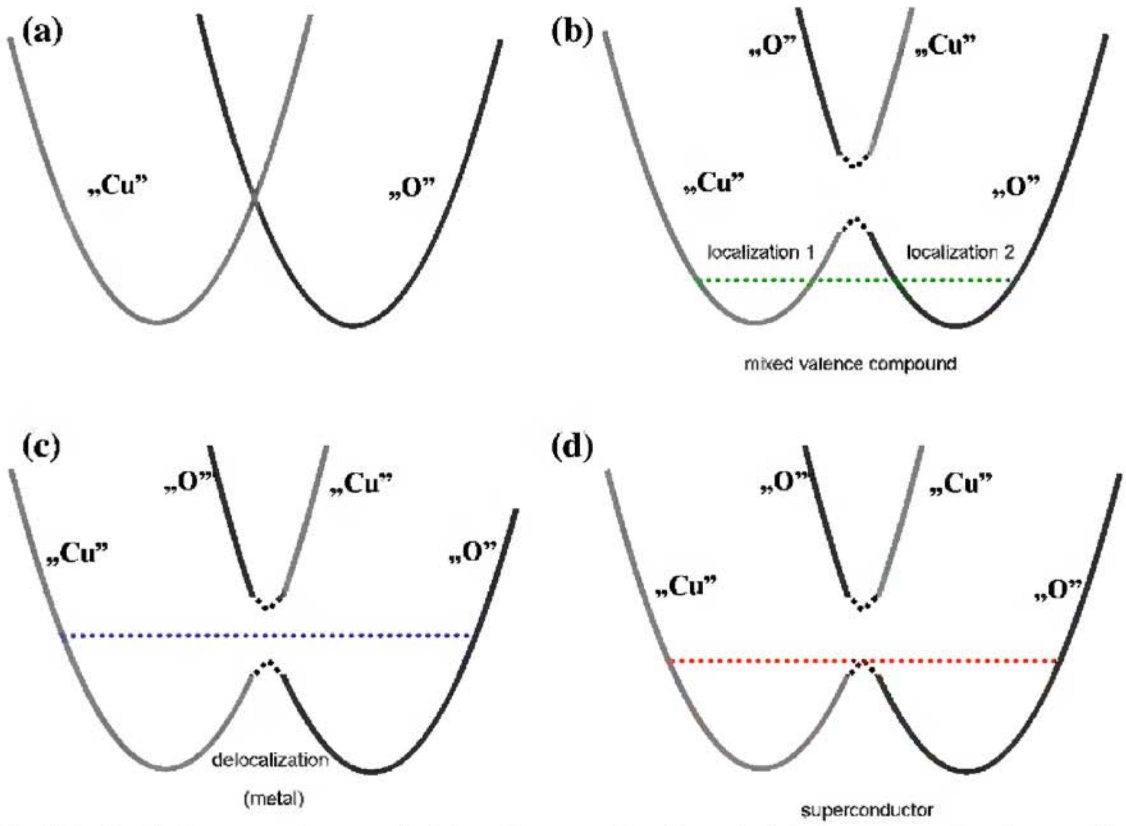

Fig. 6.21. Burdett's concept of superconductivity (scheme). (a) Two electronic diabatic energy curves (of comparable energies corresponding to their equilibrium positions) cross, resulting in two adiabatic energy curves (the ground and excited states, b,c,d). The diabatic states differ widely by the electronic charge distribution: one of them, denoted by the symbol Cu, corresponds to the electron holes on the copper atoms, while the second one, denoted by O, has such holes on the oxygen atoms. According to Burdett, the superconductivity has to do with the position of the lowest vibrational level of the ground electronic state. (b) The level is too low in energy, the vibrations are localized (either in the left- or in the right side potential energy well; this is equivalent to a quasi-degeneracy of the sum and difference of the delocalized vibrational states). The tunneling is marginal because of the exponential decay of the localized vibrational wave functions in the separating barrier. One has to do with an insulator in either of two coexisting states differing by the electronic charge distribution ("*oxidation states*")–what is known as a mixed valence compound. (c) The level is too high in energy, and the vibrations are fully delocalized and proceed in the global potential energy well. The well details do not count for much; one has to do with a state similar to averaging of the two states ("*a metallic state*"); i.e., both Cu and O have some averaged oxidation states when vibration occurs. (d) A "*magic*" position of the vibrational state, right at the height of the barrier. One may see this as two localized vibrational states that can tunnel easily through the barrier. The vibrations change the oxidation states of *Cu* and *O*; i.e., cause the electron transfer.

interesting vibration should be similar to an antisymmetric stretching vibration. In such a case, B transports an electron between the A centers. We may consider this vibration at various AA distances. If one assumes Burdett's concept, the following questions, related to the possible materials involved[86], appear:

- What would we get as the electronic charge distribution if we assume optimization of the AA distance (still keeping the constraint of linearity of ABA)? Would we get a symmetrization of

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[86] Which type of chemical compounds are most promising HTSs?

the charge distribution, as in $Na^{+\frac{1}{2}}$ F^- $Na^{+\frac{1}{2}}$ ("*averaged oxidation state*"), or we would rather obtain an asymmetric distribution like Na^+ F^- Na^0 or Na^0 F^- Na^+ ("*mixed valence compound*").
- How do the above possibilities depend on the chemical character of A and B?

Where Can We Expect Superconductivity?

Well, we do not know the answer, but there are some indications. It turned out that in the vibronic coupling[87],

- Chemical identity of A and B is very important; the strongest vibronic coupling corresponds to halogens and hydrogen (A, B ≡ F, Cl, Br, I, H).
- The strongest vibronic coupling corresponds to A=B (with the maximum for A, B ≡ F), although this condition is not the most important one.
- To exhibit the electronic instability under oscillation of B in the ABA^- radical,
  - A and B must be strongly electronegative (this may explain why oxygen is present in all the HTSs).
  - A and B must form a strong covalent bond, whereas a large overlap of the corresponding orbitals[88] is more important than the equality of their energies (cf. p. 430, Chapter 8).

6.15.3 Photostability of Proteins and DNA

How does it happen that life flourishes under protection of the Sun, whereas it is well known the star emits some deadly radiation like charged particles and UV photons? We have two main protecting targets: one is Earth's magnetic field, and the second is Earth's atmosphere. Despite the atmospheric protection, some important part of the UV radiation attains the surface of the Earth. Substances usually are not transparent for the UV, whereas absorption of a UV photon is often harmful for chemical bonds, making their dissociation or/and creating other bonds. This is desirable for producing the vitamin D_3 in our body, but in many cases, it ends badly. For example, some substances, like DNA or some important proteins, have to be completely protected because their destruction would destroy the basis of life itself. Therefore, how do these substances function so efficiently in the vibrant life processes? What represents an additional target that protects them so well?

It turns out that this wonder target is the ubiquitous hydrogen bond, an important factor determining the 3-D shape of both DNA and proteins (see p. 870). The hydrogen bond $X - H \ldots Y$ (see p. 863) has some special features that also concern its UV properties, and this

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[87] W. Grochala, R. Konecny, and R. Hoffmann, *Chem. Phys.*, *265,* 153 (2001); W. Grochala, R. Hoffmann, *New J. Chem.*, *25,* 108 (2001); W. Grochala and R. Hoffmann, *J. Phys. Chem. A*, *104,* 9740 (2000); W. Grochala and R. Hoffmann, *Pol. J. Chem.*, *75,* 1603 (2001); W. Grochala, R. Hoffmann, and P.P. Edwards, *Chem. Eur. J.*, *9,* 575 (2003); W. Grochala, *J. Mater. Chem.*, *19,* 6949 (2009).

[88] For HTSs, these orbitals are $2p$ of oxygen and $3d$ of copper.

holds independently which electronegative atoms XY are involved. The explanation of the UV protection mechanism of the hydrogen bond given below comes from Sobolewski and Domcke.[89]

Fig. 6.22 shows three electronic energy hypersurfaces for the hydrogen bond $X - H \ldots Y$, visualized as sections along the proton position coordinate that describes the position of the proton in the hydrogen bridge. The ground state S_0 (light gray) represents a diabatic state corresponding to the resonance structure $X - H \ldots Y$, in which two electrons are at X and two at Y. The energy of this singlet state has a minimum for the proton position close to X. An absorption of the UV photon makes the transition of the system to the lowest-energy singlet excited state (^1LE, dark gray) with its electronic structure denoted as $\left(X - H \ldots Y\right)^*$. Most important, its energy curve intersects another singlet excited state, which corresponds to the electron transfer from X to Y (^1CT, black). The resulting conical intersection of the states ^1LE and ^1CT is

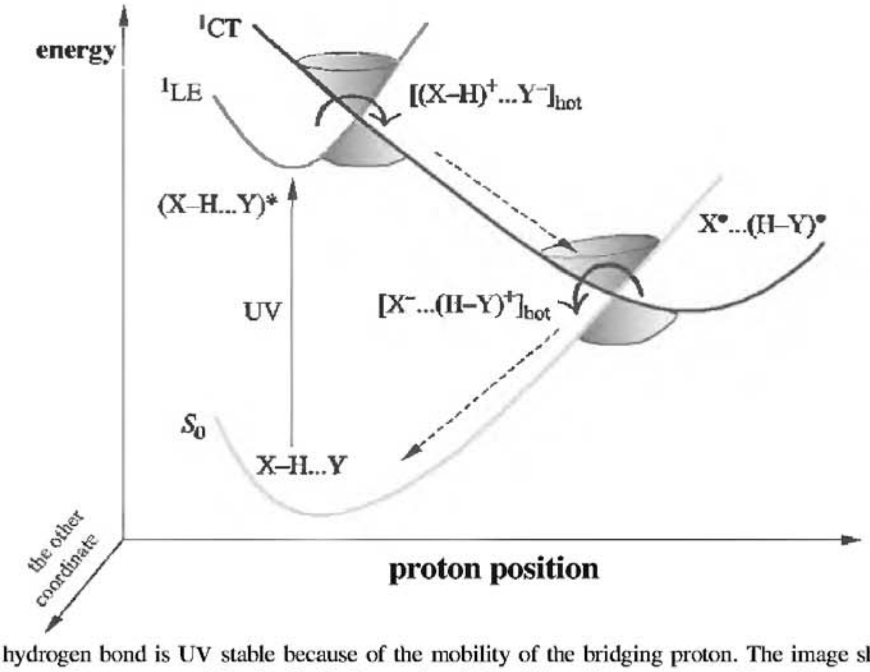

Fig. 6.22. The hydrogen bond is UV stable because of the mobility of the bridging proton. The image shows the electronic energy as a function of the proton position in the hydrogen bond $X - H \ldots Y$ (another coordinate that measures deviation of the proton from the XY axis is also marked). The electronic ground state S_0 energy curve (light gray) corresponds to the "*four-electron*" diabatic wave function corresponding to the bond pattern $X - H \ldots Y$. A UV transition to the lowest excited singlet state $\left(X - H \ldots Y\right)^*$ (^1LE, dark gray) is shown by a vertical arrow. The electronic energy curve for this state intersects (the conical intersection is shown as two cones) a singlet diabatic state (^1CT, black) that corresponds to a transfer of an electron from X to Y. The excitation energy is sufficiently large to allow the system to attain the black curve corresponding to the structure $(X - H)^+ \ldots Y^-$. After passing the conical intersection, one deals with a vibrationally excited state, which is symbolized by $\left[(X - H)^+ \ldots Y^-\right]_{hot}$. The proton continues its motion towards Y and the structure begins to be of the radical-ionic type: $X^{\bullet} \ldots (H - Y)^{\bullet}$. The system meets the second conical intersection, which allows it to attain the ground state (light gray). This time, the proton moves towards X, while its electronic energy changes to the vibrational energy of the molecule and the surrounding water. Thus, the UV photon does not harm chemical bonds, its energy goes instead to heating the surrounding water.

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[89] A. Sobolewski and W. Domcke, *Chem. Phys. Chem.*, *7*, 561 (2006).

shown as a double cone. The photon energy is large enough that the system reaches the conical intersection point and ends up on the black energy curve, which means a single electron transfer symbolized by $(X - H)^{+} \ldots Y^{-}$. Since the minimum of the black curve is shifted far to the right, after going out from the conical intersection, one has to do with a vibrational excited state denoted as an ionic "*hot*" structure: $\left[(X - H)^{+} \ldots Y^{-}\right]_{hot}$. The system slides down the black curve changing high potential energy to the vibrational energy and kinetic energy of the surrounding water molecules. This sliding down means that as the proton moves to the right, the system remains all the time in the ionic state. This, however, means there is an ion-radical structure of the type: $X^{\bullet} \ldots (H - Y)^{\bullet}$. When sliding down, the system meets the second conical intersection, which makes it possible to continue the motion on the ground-state curve (light gray). At this value of the proton position, one has the "*hot*" structure. $[X^{-} \ldots H - Y^{+}]_{hot}$. Now the sliding down means going left (the proton comes back) and transferring the vibrational energy to the water.

Therefore, the net result is the following: the absorption of the UV photon, after some bouncing of the proton in the hydrogen bridge, results in heating the surrounding water, while the hydrogen bond stays safe in its ground state.

6.15.4 Muon-Catalyzed Nuclear Fusion

Some molecules look really peculiar. They may contain a muon instead of an electron. *A muon is an unstable particle with the charge of an electron and mass equal to 207 electronic masses.*[90] For such a mass, assuming that nuclei are infinitely heavier than muon looks like a very bad approximation. Therefore, the calculations need to be non-adiabatic. The first computations for muonic molecules were performed by Kołos, Roothaan, and Sack[91] in 1960. The idea behind the project was muon-catalyzed fusion of deuterium (d) and tritium (t); the abbreviations here pertain to the nuclei only. This fascinating problem was proposed by Andrei Sakharov. Its essence is as follows.

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[90] The muon was discovered in 1937 by C.D. Anderson and S.H. Neddermeyer. Its lifetime is about $2.2 \cdot 10^{-6}$ s. The muons belong to the lepton family (with the electron and τ particle, the latter with a mass equal to about 3640 electronic masses). Nature created, for some unknown reasons, "more massive electrons". When the nuclear physicist Isidor Rabi was told about the incredible mass of the τ particle, he dramatically shouted: "*Who ordered that?!*".

[91] W. Kołos, C.C.J. Roothaan, R.A. Sack, *Rev. Mod. Phys.*, *32*, 205 (1960).

Andrei Dimitriy Sakharov (1921–1989) Russian physicist and father of the Soviet hydrogen bomb. During the final celebration of the H bomb project, Sakharov expressed his hope that the bombs would never be used. A Soviet general answered coldly that it was not scientists' business to decide such things. This was a turning point for Sakharov, and he began his fight against the totalitarian system.

The idea of muon-induced fusion was conceived by Sakharov in 1945, in his first scientific paper, under the supervision of Tamm. In 1957, David Jackson realized that muons may serve as catalysts.

If the electron in the molecule dt$e$ is replaced by a muon, immediately the dimension of the molecule decreases by a factor of about 200. How is this possible?

Well, the radius of the first Bohr orbit in the hydrogen atom (see, p. 202) is equal to $a_0 = \frac{\hbar^2}{\mu e^2}$. After introducing atomic units, this formula becomes $a_0 = \frac{1}{\mu}$, and when we take into account that the reduced mass $\mu \approx m$ (m stands for the electron mass), we get $a_0 \approx 1$. This approximation works for the electron because in reality, $\mu = 0.9995m$. If, in the hydrogen atom, we have a muon instead of an electron, then μ would equal about 250 m. This, however, means that such a "*muon Bohr radius*" would be about 250 times smaller. Nuclear forces begin to operate at such a small internuclear separation (strong interactions; see Fig. 6.23a), and are able to overcome the Coulombic barrier and stick the nuclei together by *nuclear fusion*. The muon, however, is released, and may serve as a catalyst in the next nuclear reaction.

Deuteron and tritium bound together represent a helium nucleus. One muon may participate in about 200–300 such muon-catalyzed fusion processes.[92] Everybody knows how much effort and money has been spent for decades (for the moment in vain) to ignite the nuclear synthesis $\mathrm{d} + \mathrm{t} \rightarrow \mathrm{He}$. Muon-catalyzed fusion might be an alternative solution. If the muon project were successful, humanity would have access to a practically unlimited source of energy. Unfortunately, theoretical investigations suggest that the experimental yield already achieved is about the maximum theoretical value.[93]

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[92] The commercial viability of this process will not be an option unless we can demonstrate 900 fusion events for each muon. About 10 g of deuterium and 15 g of tritium fusion would then be sufficient to supply the average person with electricity for life.

[93] This has been the subject of a joint Polish-American project. More about this may be found in K. Szalewicz, S. Alexander, P. Froelich, S. Haywood, B. Jeziorski, W. Kołos, H.J. Monkhorst, A. Scrinzi, C. Stodden, A. Velenik, and X. Zhao, in *Muon Catalyzed Fusion*, eds. S.E. Jones, J. Rafelski, H.J. Monkhorst, AIP Conference Proceedings, 181, 254 (1989).

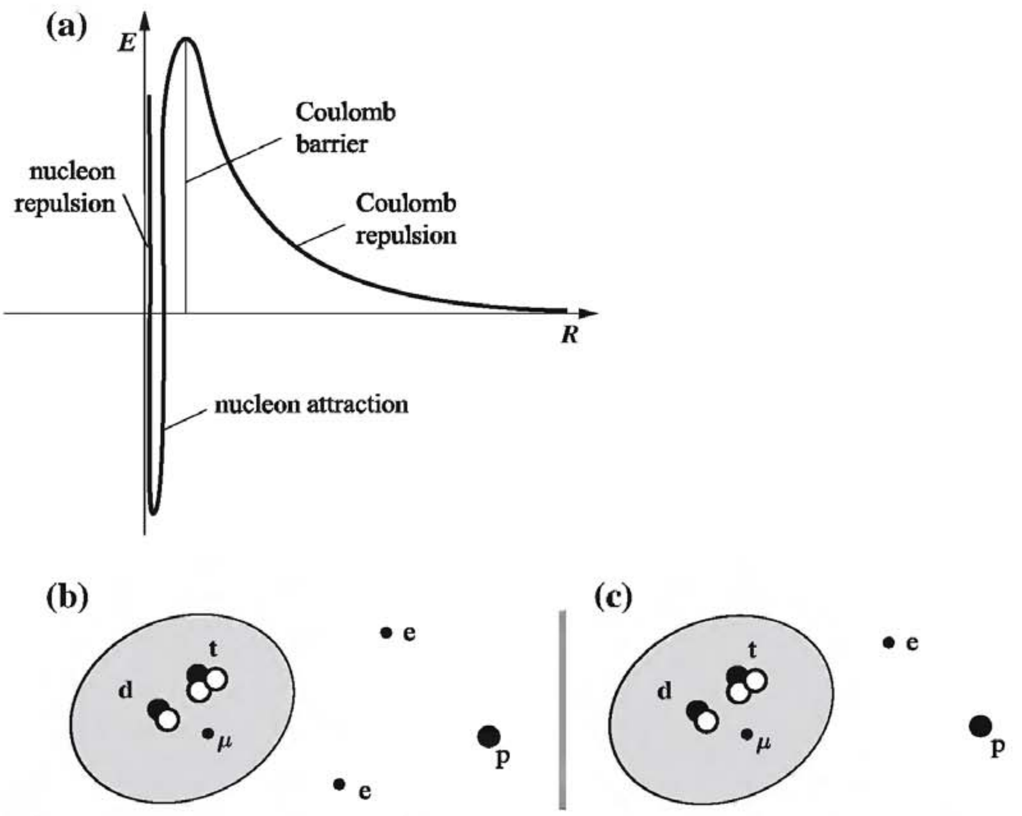

Fig. 6.23. (a) The interaction energy potential of d and t as a function of the interparticle distance (R), taking the nuclear forces into account (an outline). At large R, of the order of nanometers, we have Coulombic repulsion, at distances of the order of femtometers the internuclear attractive forces (called the *strong interaction*) are switched on and overcome the Coulombic repulsion. At a distance of a fraction of a femtometer, again we have a repulsion. (b) "*Russian dolls*" (outline): the analogs of H_2 and H_2^+.

6.15.5 "Russian Dolls," or a Molecule Within Molecule

Scrinzi and Szalewicz[94] carried out non-adiabatic calculations (p. 265) for a system of six particles: proton (p), deuterium (d), tritium (t), muon (μ), and two electrons (e) interacting by Coulombic forces (i.e., no nuclear forces are assumed). It is not easy to predict the structure of the system. It turned out that the resulting structure is a kind of "Russian doll"[95] (see Fig. 6.23b): the muon has acted according to its mass (see above) and created tdμ with a dimension of about 0.02 Å. This system may be viewed as a partly split nucleus of charge $+1$ or, alternatively, as a mini-model of the hydrogen molecular ion (scaled at 1:200). The "nucleus" serves as a partner to the proton, and both create a system similar to the hydrogen molecule, in which the two electrons play their usual binding role and the internuclear distance is about 0.7 Å. It turns out that the nonzero dimension of the "nucleus" makes a difference, and the energies computed

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[94] A. Scrinzi and K. Szalewicz, *Phys. Rev.* A, *39*, 4983 (1989).

[95] (((woman @ woman)@ woman)@)

with and without an approximation of the pointlike nucleus differ. The difference is tiny (about 0.20 meV), but it is there.

It is quite remarkable that such small effects are responsible for the fate of the total system. The authors report that the relaxation of the "nucleus" dtμ (from the excited state to the ground state[96]) causes the ionization of the system: one of the electrons flies off. Such an effect, however, may excite those who study this phenomenon. How is it possible? The "nucleus" is terribly small when seen by an electron orbiting far away. How could the electron detect that the nucleus has changed its state and that it has no future in the molecule? Here, however, our intuition fails. For the electron, the most frequently visited regions of the molecule are nuclei. We will see this in Chapter 8 (p. 444), but even the 1s state of the hydrogen atom (the maximum of the orbital is at the nucleus; see p. 201) suggests the same. Therefore, no wonder the electron *could* recognize that something has abruptly changed on one of the nuclei and (being already excited) it received much more freedom–so much, in fact, that it could leave the molecule.

We may pose an interesting question: Does the "Russian doll" represent the global minimum of the particle system? We may imagine that the proton changes its position with the deuterium or tritium; i.e., new isomers (isotopomers[97]) appear. The authors did not study this question[98], but they investigated substituting the proton with deuterium and tritium (and obtained similar results).

Scrinzi and Szalewicz also performed some calculations for an analog of H_2^+: proton, deuterium, tritium, muon, and electron. Here, the "Russian doll" looks wonderful (Fig. 6.23c); it is a four-level object:

- The molecular ion (the analog of H_2^+) is composed of *three* objects: the proton, the "split nucleus" of charge +1 and the electron.
- The "split nucleus" is also composed of *three* objects: d,t,μ (a mini-model of H_2^+).
- The tritium is composed of *three* nucleons: the proton and the two neutrons.
- Each of the nucleons is composed of *three* quarks (called the valence quarks).

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[96] A. Scrinzi and K. Szalewicz, *Phys. Rev. A., 39,* 2855 (1989). The dtμ ion is created in the rovibrational state $J = 1, v = 1$, and then the system spontaneously goes to the lower energy 01 or 00 state. The energy excess causes one electron to leave the system (ionization). This is an analog of the Auger effect in spectroscopy.

[97] The situation is quite typical, although we very rarely think this way. Some people say that they observe *two different systems*, whereas others say that they see *two states of the same system*. This begins with the hydrogen atom–it looks different in its $1s$ and $3p_z$ states. We can easily distinguish two different conformations of cyclohexane, two isomers of butane, and some chemists would say these are different substances. Going much further, N_2 and CO represent two different molecules, or is one of them nothing but an excited state of the other? However strange it may sound for a chemist, N_2 represents an excited state of CO because we may imagine a nuclear reaction of the displacement of a proton from one nitrogen to the other (and the energy curve per nucleon as a function of the atomic mass is convex). Such a point of view is better for viewing each object as a "new animal": it enables us to see and use some relations among these animals.

[98] They focused their attention on tdμ.

Summary

- In the adiabatic and the Born-Oppenheimer approximations, the total wave function is taken as a product $\Psi = \psi_k(\boldsymbol{r}; R) f_k(\boldsymbol{R})$ of the function $f_k(\boldsymbol{R})$, which describes the motion of the nuclei (vibrations and rotations) and the function $\psi_k(\boldsymbol{r}; R)$ that pertains to the motion of electrons (and depends parametrically on the configuration of the nuclei; here, we give the formulas for a diatomic molecule). This approximation relies on the fact that the nuclei are thousands of times heavier than the electrons.
- The function $\psi_k(\boldsymbol{r}; R)$ represents an eigenfunction of the electronic Hamiltonian $\hat{H}_0(R)$; i.e., the Hamiltonian $\hat{H}$, in which the kinetic energy operator for the nuclei is assumed to be zero (the *clamped nuclei Hamiltonian*)
- The eigenvalue of the clamped nuclei Hamiltonian depends on positions of the nuclei and in the Born-Oppenheimer approximation, it is mass-independent. This energy as a function of the configuration of the nuclei represents the potential energy for the motion of the nuclei (Potential Energy Surface, or PES).
- The function $f_k(\boldsymbol{R})$ is a product of a spherical harmonic[99] Y_J^M that describes the rotations of the molecule (J and M stand for the corresponding quantum numbers) and a function that describes the vibrations of the nuclei.
- The diagram of the energy levels shown in Fig. 6.4 represents the basis of molecular spectroscopy. The diagram may be summarized in the following way:
  - The energy levels form some series separated by energy gaps, with no discrete levels. Each series corresponds to a single electronic state k, and the individual levels pertain to various vibrational and rotational states of the molecule in electronic state k.
  - Within the series for a given electronic state, there are groups of energy levels, each group characterized by a distinct vibrational quantum number ($v = 0, 1, 2, \ldots$), and within the group, the states of higher and higher energies correspond to the increasing rotational quantum number J.
  - The energy levels fulfill some general relations:
    - Increasing k corresponds to an electronic excitation of the molecule (UV-VIS, ultraviolet and visible spectrum).
    - Increasing v pertains to a vibrational excitation of the molecule, and requires the energy to be smaller by one or two orders of magnitude than an electronic excitation (IR, infrared spectrum).
    - Increasing J is associated with energy smaller by one or two orders of magnitude than a vibrational excitation (microwaves).
- Above the dissociation limit, one is dealing with a continuum of states of the dissociation products with kinetic energy. In such a continuum, one may have also the resonance states, which may have wave functions that resemble those of stationary states but differ from them by having finite lifetimes.
- The electronic wave functions $\psi_k(\boldsymbol{r}; R)$ correspond to the energy eigenstates $E_k^0(R)$, which are functions of R. The energy curves[100] $E_k^0(R)$ for different electronic states k may cross each other, unless the molecule is diatomic and the two electronic states have the same symmetry.[101] In such a case, we have what is known as an avoided crossing (see Figs. 6.15 and 6.16).
- The adiabatic states represent the eigenfunctions of $\hat{H}_0(R)$. If electrons have enough time to follow the nuclei, we may apply the adiabatic function (which may change its chemical character when varying R). The diabatic states are not the eigenfunctions of $\hat{H}_0(R)$ and preserve their chemical character when changing R. If electrons are too slow to follow the nuclei, changing R may result in keeping the same chemical character of the solution (diabatic state). In the adiabatic and diabatic approaches, the motion of the nuclei is described using a single PES.
- The non-adiabatic approach requires using several or many PESs when describing motion of the nuclei. The total wave function is a linear combination of the rovibronic functions with different and R-dependent amplitudes.

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[99] This refers to the eigenfunction for the rigid rotator.

[100] These curves are expressed as functions of R.

[101] That is, they transform according to the same irreducible representation.

- For polyatomic molecules, the energy hypersurfaces $E_k^0(\boldsymbol{R})$ can cross. The most important is the *conical intersection* (Fig. 6.19) of the two (I and II) diabatic hypersurfaces; i.e., those that (each individually) preserve a given pattern of chemical bonds. This intersection results in two adiabatic hypersurfaces ("*lower PES and upper PES*"). Each of the adiabatic hypersurfaces consists of two parts: one belonging to I and the second to II. Using a suitable coordinate system in the configurational space, we obtain the adiabatic hypersurface splitting (the difference of E_- and E_+) when changing two coordinates (ξ_1 *and* ξ_2) only (the branching plane). The splitting begins by a linear dependence on ξ_1 and ξ_2, which gives a sort of cone (hence the name *conical intersection*). The other coordinates (the seam space) alone are unable to cause the splitting, although they may influence the opening angle of the cone.
- Conical intersection plays a prominent role in the photochemical reactions because the excited molecule slides down the upper adiabatic hypersurface to the funnel (just the conical intersection point) and then, with a yield close to 100%, lands on the lower adiabatic hypersurface (assuming that there is a mechanism for dissipation of the excess energy).
- The vibronic effects are the basis of many important phenomena.

Main Concepts, New Terms

adiabatic approach (p. 302)
adiabatic approximation (p. 268)
asymmetric top (p. 293)
avoided crossing (p. 306)
Berry phase (p. 314)
BFCS (p. 289)
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From the Research Front

For the hydrogen molecule, one may currently get a very high accuracy in predicting rovibrational levels. For example, exact analytic formulas have been derived[102] that allow one to compute the Born-Oppenheimer potential with the uncertainty smaller than 10^{-9} cm^{-1} and add the correction for the nonzero size of each nucleus (the latter correction shifts the rovibrational energy levels by less than 10^{-4} cm^{-1} in all cases). The approach presented on p. 275 is able to produce the adiabatic diagonal correction, and the non-adiabatic corrections for all rovibrational states of the ground electronic state with the accuracy better than 10^{-4} cm^{-1}. One is able to test the accuracy of not only the theory given in this chapter, but also of its most sophisticated extensions, including quantum electrodynamics (QED). One may say that virtually for the first time, QED can be confronted with the most accurate experiments beyond the traditional territory of the free electron and simple atoms (hydrogen, helium, lithium); i.e., for systems with more than one nucleus. For the hydrogen molecule, one starts with an accurate solution to the Schrödinger equation[103] and then, circumventing the Dirac equation, one includes all the relativistic Breit-Pauli terms [all terms of the order of $\left(\frac{1}{c}\right)^2$, the terms of the order of $\frac{1}{c}$ vanish, where 137.0359991 a.u.] and later, the complete QED corrections of the order of $\left(\frac{1}{c}\right)^3$ and the leading terms of $\left(\frac{1}{c}\right)^4$. Just to show the accuracy achieved for the hydrogen molecule, for the $J = 0 \rightarrow 1$ rotational excitation, the theory gives[104] 118.486812(9) cm^{-1}, while the most accurate experiment to date[105] gives 118.48684(10) cm^{-1}. Some theories trying to explain the presence of black matter need the nuclear forces operating at larger distances than they are traditionally believed to do. If these theories were true, there would be no such agreement between the theory and experiment, and we would see a larger difference.

Ad Futurum

The computational effort needed to calculate the PES for an M atomic molecule is proportional to 10^{3M-6}. This strong dependence suggests that, for the next 20 years, it would be unrealistic to expect high-quality PES computations for $M > 10$. However, experimental chemistry offers high-precision results for molecules with hundreds of atoms. It seems inevitable that it will be possible to freeze the coordinates of many atoms. There are good reasons for such an approach: indeed, most atoms play the role of spectators in chemical processes. It may be that limiting ourselves to, say, 10 atoms will make the computation of rovibrational spectra feasible.

Additional Literature

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[106] We have chosen the center of the *ab* bond.

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Questions

1. The non-adiabatic theory for a diatomic ($\mathbf{r}$ denotes the electronic coordinates, $\mathbf{R}$ stands for the vector connecting nucleus b with nucleus a, $R \equiv |\mathbf{R}|$, N means the number of electrons, m is the electron mass, V represents the Coulombic interaction of all particles, μ is the reduced mass of the two nuclei of masses M_a and M_b).
   a. the total wave function can be represented as $\Psi(\mathbf{r}, \mathbf{R}) = \sum_k \psi_k(\mathbf{r};\, R) f_k(\mathbf{R})$, where the functions ψ_k form a complete set in the Hilbert space for electrons (at a given R), and f_k are the coefficients depending on $\mathbf{R}$
   b. in the expression $\Psi(\mathbf{r}, \mathbf{R}) = \sum_k \psi_k(\mathbf{r};\, R) f_k(\mathbf{R})$ the functions $f_k(\mathbf{R})$ describe rotations and vibrations of the molecule
   c. as functions $\psi_k(\mathbf{r};\, R)$ one may assume the eigenfunctions of the electronic Hamiltonian
   d. may provide only some approximation of the solution to the Schrödinger equation
2. Adiabatic approximation (notation as in question 1).
   a. is also known as the Born-Oppenheimer approximation
   b. the electronic Hamiltonian can be obtained from the total Hamiltonian by neglecting the kinetic energy operator for the nuclei
   c. in the adiabatic approximation the total wave function represents a product $\psi_k(\mathbf{r};\, \mathbf{R}) f_k(\mathbf{R})$, where $\psi_k(\mathbf{r};\, \mathbf{R})$ stands for the eigenfunction of the clamped nuclei Hamiltonian for the configuration of the nuclei given by $\mathbf{R}$, while $f_k(\mathbf{R})$ denotes the wave function for the motion of the nuclei
   d. E_k^0 as a function of $\mathbf{R}$ represents the eigenvalue of the clamped nuclei Hamiltonian that corresponds to the wave function $\psi_k(\mathbf{r};\, \mathbf{R})$.
3. A diatomic in the adiabatic approximation, the origin of the coordinate system is in the geometric center of the molecule (at $\mathbf{R}/2$). The nuclei vibrate in the potential:
   a. $E_k^0(R) + J(J+1)\frac{\hbar^2}{2\mu R^2}$
   b. $\left\langle \psi_k | \hat{H} \psi_k \right\rangle + (2J+1)\frac{\hbar^2}{2\mu R^2}$
   c. $E_k^0(R) + H'_{kk} + J(J+1)\frac{\hbar^2}{2\mu R^2}$
   d. $\left\langle \psi_k | \hat{H} \psi_k \right\rangle + J(J+1)\frac{\hbar^2}{2\mu R^2}$
4. The potential energy curves for the motion of the nuclei for electronic states computed at the Born-Oppenheimer approximation for diatomics
   a. may not intersect
   b. have to intersect at an internuclear distance
   c. cannot intersect, if the corresponding eigenfunctions belong to the same irreducible representation of the symmetry group of the Hamiltonian
   d. may intersect, if the corresponding wave functions are of different symmetry.
5. The potential energy for the motion of the nuclei in the Born-Oppenheimer approximation:
   a. contains the eigenvalue of the clamped nuclei Hamiltonian
   b. as a function of the configuration of the nuclei may exhibit many minima
   c. contains the electronic energy
   d. does not change after rotational excitations

6. Due to the rotational excitation $J \rightarrow (J+1)$ of a diatomic of bond length R
   a. one has to add to the potential energy a term proportional to $(2J+1)R^2$
   b. the potential energy for vibrations changes
   c. the molecule may dissociate due to the centrifugal force
   d. the momentum of the molecule increases
7. The adiabatic approximation
   a. takes into account the finite mass of the nuclei
   b. means the total wave function being a product of the electronic wave function and a wave function that describes the motion of the nuclei
   c. as a consequence leads to the concept of a spatial shape of a molecule
   d. is better satisfied by a molecule with muons instead of electrons.
8. Basics of spectroscopy within the Born-Oppenheimer approximation.
   a. the electronic structure changes after absorbing microwaves
   b. to excite vibrational levels (preserving the electronic state) one needs the IR radiation
   c. a red sweater witnesses about a dye that absorbs red light
   d. microwaves can excite rotations of polar molecules.
9. At the conical intersection, the following directions in the space of the nuclear configurations make splitting of E_+ and E_-
   a. $\nabla(\bar{E}_1 - \bar{E}_2)$ and $\nabla(V_{12})$
   b. $\nabla(\frac{\bar{E}_1+\bar{E}_2}{2})$ and $\nabla(V_{12})$
   c. $\nabla(\frac{\bar{E}_1-\bar{E}_2}{2})$ and $\nabla(V_{12})$
   d. any direction in the branching space.
10. At the conical intersection the opening angle of the cone
    a. equals zero
    b. in general differs along the directions of $\nabla(\bar{E}_1 - \bar{E}_2)$ and $\nabla(V_{12})$
    c. depends on the point of the seam space
    d. in the Born-Oppenheimer approximation is the same for different isotopomers.

Answers

1a,b,c, 2b,c,d, 3c,d, 4a,c,d, 5a,b,c 6b,c, 7b,c, 8b,d, 9a,c,d 10b,c,d