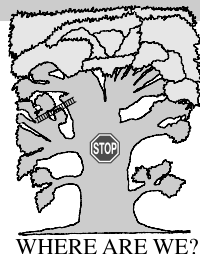


Chapter 6

SEPARATION OF ELECTRONIC AND NUCLEAR MOTIONS



Where are we?

We are on the *most important* branch of the TREE.

An example

A colleague shows us the gas phase absorption spectra of the hydrogen atom and of the hydrogen molecule recorded in the ultraviolet and visible (UV-VIS), infrared (IR) and microwave range. The spectrum of the hydrogen atom consists of separated narrow absorption lines. The hydrogen molecule spectrum is much more complex, instead of the absorption lines we have some absorption bands with a regular and mysterious structure. If the theory given in the previous chapters is correct, then it should explain why these bands appear and why the spectra have such a strange structure.

What is it all about

Separation of the centre-of-mass motion (▲)

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- Space-fixed coordinate system (SFCS)
- New coordinates
- Hamiltonian in the new coordinates
- After separation of the centre-of-mass motion

Exact (non-adiabatic) theory (Ⓢ)

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Adiabatic approximation (▲)

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Born–Oppenheimer approximation (▲)

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Oscillations of a rotating molecule (Δ)

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- One more analogy
- The fundamental character of the adiabatic approximation – PES

Basic principles of electronic, vibrational and rotational spectroscopy (Δ)

p. 235

- Vibrational structure
- Rotational structure

Approximate separation of rotations and vibrations (Δ)

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Polyatomic molecule (Ⓢ♦)

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- Kinetic energy expression
- Simplifying using Eckart conditions

• Approximation: decoupling of rotation and vibrations	
• The kinetic energy operators of translation, rotation and vibrations	
• Separation of translational, rotational and vibrational motions	
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• “Russian dolls” – or a molecule within molecule	

Nuclei are thousands times heavier than the 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 a lot 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 3D space.*

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

Why is it 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 3D structure with the nuclei occupying some positions in 3D space, with chemical bonds etc. This is why the present chapter occupies the *central* position on the TREE.

What is needed?

- Postulates of quantum mechanics (Chapter 1, needed).
- Separation of the centre-of-mass motion (Appendix I on p. 971, necessary).
- Rigid rotator (Chapter 4, necessary).
- Harmonic and Morse oscillators (Chapter 4, necessary).
- Conclusions from group theory (Appendix C, p. 903, advised).

¹It does not mean that the electrons and the 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.

Classical papers

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 same famous Lutheran High School in Budapest as Jenő Pál (who later used the name Eugene) Wigner. In 1926 von Neumann received his chemistry engineering diploma, and in the same year he completed his PhD in mathematics at the University of Budapest. He finally emigrated to the USA and founded the Princeton Advanced Study Institute. John von Neumann was a mathematical genius. He contributed to the mathematical foundations of quantum theory, computers, and game theory. Von Neumann made a strange offer of a professor-



ship at the Advanced Study Institute to Stefan Banach from the John Casimir University in Lwów. He handed him a cheque with a handwritten figure “1” and asked Banach to add as many zeros as he wanted. “*This is not enough money to persuade me to leave Poland*” – answered Banach.

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 (1929) 465 and “*Über das Verhalten von Eigenwerten bei adiabatischen Prozessen*” also published in *Physikalische Zeitschrift*, 30 (1929) 467, and later in a paper by Edward Teller published in the *Journal of Chemical Physics*, 41 (1937) 109. ★ A fundamental approximation (called the Born–Oppenheimer approximation) has been introduced in the paper “*Zur Quantentheorie der Molekeln*” by Max Born and Julius Robert Oppenheimer in *Annalen der Physik*, 84 (1927) 457, which follows from the fact that nuclei are much heavier than electrons. ★ Gerhard Herzberg was the greatest spectroscopist of the XX 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).

Edward Teller (1908–2004), American physicist of Hungarian origin, professor at the George Washington University, the University of Chicago and the University of California. Teller left Hungary in 1926, received his PhD in 1930 at the University of Leipzig, and fled Nazi Germany in 1935. Teller was the project leader and the top brain behind the American hydrogen bomb project in Los Alamos, believing that this was the way to overthrow communism. The hydrogen bomb patent is owned by Edward Teller and Stanisław Ulam. Interrogated on Robert Oppenheimer’s possible contacts with Soviet Intelligence Service, he de-



clared: “*I feel I would prefer to see the vital interests of this country in hands that I understand better and therefore trust more*”.

Eugene Paul Wigner (1902–1995), American chemist, physicist and mathematician of Hungarian origin, professor at the Princeton University (USA). At the age of 11 Wigner, a primary 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 he did not have tuberculosis). In 1915 Wigner entered the famous Lutheran High School in Budapest. Fulfilling the wish 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 PhD 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 tan-



nery. . . Accidentally 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*".

★ The world's first computational papers using a rigorous approach to go beyond the Born–Oppenheimer approximation for molecules were two articles by Włodzimierz Kołos and Łutostław Wolniewicz, the first in *Acta Physica Polonica* 20 (1961) 129 entitled "*The Coupling between Electronic and Nuclear Motion and the Relativistic Effects in the Ground State of the H_2 Molecule*" and the second in *Physics Letters*, 2 (1962) 222 entitled "*A Complete Non-Relativistic Treatment of the H_2 Molecule*". ★ The discovery of the conical intersection and the funnel effect in photochemistry is attributed to Howard E. Zimmerman [*Journal of the American Chemical Society*, 88 (1966) 1566²] and to Josef Michl [*Journal of Molecular Photochemistry*, 243 (1972)]. Important contributions in this domain were also made by Lionel Salem and Christopher Longuet-Higgins.

Christopher Longuet-Higgins, 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.

²The term "funnel effect" was coined in this paper.

6.1 SEPARATION OF THE CENTRE-OF-MASS MOTION

6.1.1 SPACE-FIXED COORDINATE SYSTEM (SFCS)

Let us consider first a diatomic molecule with the nuclei labelled by a, b , and n electrons. Let us choose a Cartesian coordinate system in our laboratory (called the space-fixed coordinate system, SFCS) with the origin located at an arbitrarily chosen point and with arbitrary orientation of the axes.³ The nuclei have the following positions: $\mathbf{R}_a = (X_a, Y_a, Z_a)$ and $\mathbf{R}_b = (X_b, Y_b, Z_b)$, while electron i has the coordinates x'_i, y'_i, z'_i .

We write the Hamiltonian for the system (Chapter 1):

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2M_a}\Delta_a - \frac{\hbar^2}{2M_b}\Delta_b - \sum_{i=1}^n \frac{\hbar^2}{2m}\Delta'_i + V, \quad (6.1)$$

where the first two terms stand for the kinetic energy operators of the nuclei (with masses M_a and M_b), the third term corresponds to the kinetic energy of the electrons (m is the electron mass, all Laplacians are in the space-fixed coordinate system), and V denotes the Coulombic potential energy operator (interaction of all the particles, nuclei–nuclei, nuclei–electrons, electrons–electrons; $Z_a e$ and $Z_b e$ are nuclear charges)

$$V = \frac{Z_a Z_b e^2}{R} - Z_a \sum_i \frac{e^2}{r_{ai}} - Z_b \sum_i \frac{e^2}{r_{bi}} + \sum_{i < j} \frac{e^2}{r_{ij}}. \quad (6.2)$$

When 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 centre-of-mass, then forget about the motion and focus on the rest, i.e. on the *relative* motion of the particles.

6.1.2 NEW COORDINATES

The total mass of the molecule is $M = M_a + M_b + mn$. The components of the centre-of-mass position vector are⁴

$$\begin{aligned} X &= \frac{1}{M} \left(M_a X_a + M_b X_b + \sum_i m x'_i \right), \\ Y &= \frac{1}{M} \left(M_a Y_a + M_b Y_b + \sum_i m y'_i \right), \\ Z &= \frac{1}{M} \left(M_a Z_a + M_b Z_b + \sum_i m z'_i \right). \end{aligned}$$

³For example, right in the centre of the Norwich market square.

⁴Do not mix the coordinate Z with the nuclear charge Z .

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 on p. 971, choice II):

- three centre-of-mass coordinates X, Y, Z ,
- three components of the vector $\mathbf{R} = \mathbf{R}_a - \mathbf{R}_b$ that separates 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 $i = 1, 2, \dots, n$, which show the electron's position with respect to the *geometric centre*⁵ of the molecule.

6.1.3 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. First (similarly as in Appendix I), 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 similarly 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 similarly for y'_i and z'_i .

⁵If the origin were chosen in the centre of mass instead of the geometric centre, V becomes mass-dependent (J. Hinz, A. Alijah and L. Wolniewicz, *Pol. J. Chem.* 72 (1998) 1293), cf. also Appendix I, Example II. We want to avoid this.

Now, let us create the second derivative operators:

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

After inserting all this into the Hamiltonian (6.1) we obtain the Hamiltonian expressed in the new coordinates:⁶

clamped nuclei
Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta_{XYZ} + \hat{H}_0 + \hat{H}', \quad (6.3)$$

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

electronic
Hamiltonian

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

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

$$\hat{H}' = -\frac{\hbar^2}{2\mu} \Delta_R + \hat{H}'' \quad (6.5)$$

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

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

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

⁶The potential energy also has to be expressed using the new coordinates.

The \hat{H}_0 does not contain the kinetic energy operator of the nuclei, but all the other terms (this is why it is called the electronic 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. $-\frac{\hbar^2}{2\mu}\Delta_{\mathbf{R}}$, denotes the kinetic energy operator of the nuclei,⁷ while the operator \hat{H}'' couples the motions of the nuclei and electrons.⁸

6.1.4 AFTER SEPARATION OF THE CENTRE-OF-MASS MOTION

After separation of the centre-of-mass motion (the first term in eq. (6.3) is gone, see Appendix I on p. 971) we obtain the eigenvalue problem of the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}'. \quad (6.6)$$

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 form⁹

⁷What moves is a particle of reduced mass μ and coordinates R_x, R_y, 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 \mathbf{R}), as well as its rotations (changes in orientation of \mathbf{R}).

⁸The first of these two terms contains the reduced mass of the two nuclei, where ∇_i denotes the nabla operator for *electron* i , $\nabla_i \equiv i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$ with i, j, k being the unit vectors along the axes x, y, z . The second term is non-zero only for the heteronuclear case and contains the mixed product of nablas: $\nabla_R \nabla_i$ with $\nabla_R = i \frac{\partial}{\partial R_x} + j \frac{\partial}{\partial R_y} + k \frac{\partial}{\partial R_z}$ and R_x, R_y, R_z as the components of the vector \mathbf{R} .

⁹Where did 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. 202). 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 $\{\bar{\psi}_k(\mathbf{r})\}$, and the second on the nuclear coordinates $\{\bar{\phi}_l(\mathbf{R})\}$. The complete basis set for the Hilbert space of our system could be constructed as a Cartesian product $\{\bar{\psi}_k(\mathbf{r})\} \times \{\bar{\phi}_l(\mathbf{R})\}$, i.e. all possible product-like functions $\bar{\psi}_k(\mathbf{r})\bar{\phi}_l(\mathbf{R})$. Thus, the wave function could be expanded in a series

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{kl} c_{kl} \bar{\psi}_k(\mathbf{r}) \bar{\phi}_l(\mathbf{R}) = \sum_k \bar{\psi}_k(\mathbf{r}) \left[\sum_l c_{kl} \bar{\phi}_l(\mathbf{R}) \right] = \sum_k \bar{\psi}_k(\mathbf{r}) f_k(\mathbf{R}),$$

where $f_k(\mathbf{R}) = \sum_l c_{kl} \bar{\phi}_l(\mathbf{R})$ stands for a to-be-sought coefficient depending on \mathbf{R} (rovibrational function). If we had to do 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 $\bar{\psi}_k(\mathbf{r})\bar{\phi}_l(\mathbf{R})$ 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

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_k^{\mathcal{N}} \psi_k(\mathbf{r}; R) f_k(\mathbf{R}), \quad (6.7)$$

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

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

that depend parametrically¹⁰ on the internuclear distance R , and $f_k(\mathbf{R})$ are yet unknown rovibrational functions (describing the rotations and vibrations of the molecule).

Derivation

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

$$(\hat{H}_0 + \hat{H}') \sum_k^{\mathcal{N}} \psi_k(\mathbf{r}; R) f_k(\mathbf{R}) = E \sum_k^{\mathcal{N}} \psi_k(\mathbf{r}; R) f_k(\mathbf{R}). \quad (6.9)$$

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

$$\sum_k^{\mathcal{N}} \langle \psi_l | (\hat{H}_0 + \hat{H}') (\psi_k f_k) \rangle_e = E \sum_k^{\mathcal{N}} \langle \psi_l | \psi_k \rangle_e f_k. \quad (6.10)$$

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

$$E_l^0 f_l + \sum_k^{\mathcal{N}} \langle \psi_l | \hat{H}' (\psi_k f_k) \rangle_e = E f_l. \quad (6.11)$$

Now, let us focus on the expression $\hat{H}'(\psi_k f_k) = -\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}}(\psi_k f_k) + \hat{H}''(\psi_k f_k)$, which we have in the integrand in eq. (6.11). Let us concentrate on the first of

have only a few, to be exact only one such term. If so, it would be reasonable to introduce a *parametric dependence* of the function $\psi_k(\mathbf{r})$ 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 are such and such, and how they behave, when the distances are changed.*

¹⁰For each value of R we have a different formula for ψ_k .

these terms¹¹

$$\begin{aligned}
 -\frac{\hbar^2}{2\mu}\Delta_{\mathbf{R}}(\psi_k f_k) &= -\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}(\psi_k f_k) = -\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}[\psi_k\nabla_{\mathbf{R}}f_k + (\nabla_{\mathbf{R}}\psi_k)f_k] \\
 &= -\frac{\hbar^2}{2\mu}[\nabla_{\mathbf{R}}\psi_k\nabla_{\mathbf{R}}f_k + \psi_k\Delta_{\mathbf{R}}f_k + (\Delta_{\mathbf{R}}\psi_k)f_k + \nabla_{\mathbf{R}}\psi_k\nabla_{\mathbf{R}}f_k] \\
 &= -\frac{\hbar^2}{2\mu}[2(\nabla_{\mathbf{R}}\psi_k)(\nabla_{\mathbf{R}}f_k) + \psi_k\Delta_{\mathbf{R}}f_k + (\Delta_{\mathbf{R}}\psi_k)f_k]. \quad (6.12)
 \end{aligned}$$

After inserting the result into $\langle\psi_l|\hat{H}'(\psi_k f_k)\rangle_e$ and recalling eq. (6.5) we have

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

with

$$H'_{lk} \equiv \langle\psi_l|\hat{H}'\psi_k\rangle_e.$$

We obtain the following form of (6.11)

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

(we have profited from the equality $\langle\psi_k|\nabla_{\mathbf{R}}\psi_k\rangle_e = 0$, which follows from the differentiation of the normalization condition¹² for the function ψ_k)

Non-adiabatic nuclear motion

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

¹¹We use the relation $\Delta_{\mathbf{R}} = (\nabla_{\mathbf{R}})^2$.

¹²We assume that the phase of the wave function $\psi_k(\mathbf{r}; R)$ does not depend on R , i.e. $\psi_k(\mathbf{r}; R) = \tilde{\psi}_k(\mathbf{r}; R) \exp(i\phi)$, where $\tilde{\psi}_k$ is a real function and $\phi \neq \phi(R)$. This immediately gives $\langle\psi_k|\nabla_{\mathbf{R}}\psi_k\rangle_e = \langle\tilde{\psi}_k|\nabla_{\mathbf{R}}\tilde{\psi}_k\rangle_e$, which is zero from differentiating the normalization condition. Indeed, the normalization condition: $\int \psi_k^2 d\tau_e = 1$. Hence, $\nabla_{\mathbf{R}} \int \psi_k^2 d\tau_e = 0$, or $2 \int \psi_k \nabla_{\mathbf{R}} \psi_k d\tau_e = 0$.

Without this approximation we will surely have trouble.

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + E_l^0(R) + H'_{ll}(R) - E \right] f_l = - \sum_{k(\neq l)}^{\mathcal{N}} \Theta_{lk} f_k, \quad (6.14)$$

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

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

Note, that the operator H'_{lk} depends on the length of the vector \mathbf{R} , but not on its direction.¹³

Eq. (6.14) is equivalent to the Schrödinger equation.

Eqs. (6.14) and (6.15) have been derived under the assumption that ψ_k of eq. (6.7) satisfy (6.8). If instead of $\psi_k(\mathbf{r}; R)$ we use a (generally non-orthogonal) complete set $\{\psi_k(\mathbf{r}; R)\}$ in (6.7), eqs. (6.14) and (6.15) would change to

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + \bar{E}_l(R) + H'_{ll}(R) - E \right] f_l = - \sum_{k(\neq l)}^{\mathcal{N}} \Theta_{lk} f_k, \quad (6.16)$$

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

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

and $\bar{E}_l(R) \equiv \langle \bar{\psi}_l | \hat{H}_0 \bar{\psi}_l \rangle_e$.

6.3 ADIABATIC APPROXIMATION

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

$$\left[-\frac{\hbar^2}{2\mu} \Delta_{\mathbf{R}} + E_l^0(R) + H'_{ll}(R) \right] f_l = E f_l, \quad (6.18)$$

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

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

diagonal
correction

¹³This 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.

$$\Psi \approx \psi_I(\mathbf{r}; \mathbf{R}) f_I(\mathbf{R}). \quad (6.19)$$

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

A simple analogy

Let us stop for a while to catch the 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.¹⁴ 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 miles, the beloved Alps move a tiny, tiny distance, so that 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 for example, 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 of years), the mountains will be 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 *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 \mathbf{r} at a given configuration of the mountains \mathbf{R} can be *approximated*¹⁵ by a product of the probability of finding the mountains at this configuration $|f_I(\mathbf{R})|^2 d^3\mathbf{R}$ and the probability $|\psi_I(\mathbf{r}; \mathbf{R})|^2 d^3\mathbf{r}$ of finding the tourist in the position shown by the vector \mathbf{r} , when the mountains have this particular configuration \mathbf{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 point: the Alps do not move in the potential created by tourists, the dominant geological processes are tourist-independent. As we will soon see, nuclear motion is dictated by the potential *which is the electronic energy*.

¹⁴The continental plates collide like billiard balls in a kind of quasi-periodic oscillation. During the current oscillation, the India plate which moved at 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. Europe was hit from the South by a few plates moving at about 4 cm a year, and this is why we have much lower Alps. While visiting the Atlantic coast of Maine (USA), I thought that the colour of the rocks was very similar to those I remembered from Brittany (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.

¹⁵This is an approximation, because in the non-adiabatic, i.e. fully correct, approach the total wave function is a superposition of many such products, eq. (6.7), corresponding to various electronic and rovibrational wave functions.

6.4 BORN–OPPENHEIMER APPROXIMATION

In the adiabatic approximation, $H'_{ll} = \int \psi_l^* H' \psi_l d\tau_e$ represents a small correction to $E_l^0(R)$. *Neglecting the correction results in the Born–Oppenheimer approximation*

$$H'_{ll} \cong 0.$$

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

Julius Robert Oppenheimer (1904–1967), American physicist, professor at the University of California in Berkeley and the California Institute of Technology in Pasadena, and at the Institute for Advanced Study in Princeton. In 1943–1945 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 Ger-



many, and worked with Born, developing what has been known as the Born–Oppenheimer approximation."

6.5 OSCILLATIONS 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 $f_k(\mathbf{R}) = f_k(R, \theta, \phi)$ 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

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

No additional approximation is introduced. We say only that the isolated molecule vibrates absolutely independently of whether it is oriented towards the Capricorn or Taurus Constellations (space is isotropic). The function $\chi_k(R)$ is yet unknown, therefore dividing by R in (6.20) is meaningless.¹⁶

¹⁶In the case of polyatomics the function $f_k(\mathbf{R})$ 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. 63).

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

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

After inserting the Laplacian (in spherical coordinates, see Appendix H on p. 969) and the product (6.20) into (6.18) we obtain the following series of transformations

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

Look! The left-hand side only depends on R , and the right-hand 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

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

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

Now, we are amazed to see that (6.23) is *identical* (cf. p. 176) 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. 176 mathematicians have proved that this equation has a solution only if $\lambda = -J(J+1)$, where $J = 0, 1, 2, \dots$. Since Y stands for the rigid rotator wave function, which we know very well, we now concentrate exclusively on the function χ_k , which describes vibrations (changes in the length of \mathbf{R}).

After inserting the permitted values of λ into (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

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

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

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

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

centrifugal force
effect

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) approximations are applied.

If the $H'_{kk}(R)$ term were not present in $V_{kJ}(R)$ (as it is in the Born–Oppenheimer approximation), then the potential energy would not depend on the mass of the nuclei.

Therefore, in the Born–Oppenheimer approximation the potential energy is the same for H_2 , HD and D_2 .

It is worth noting that $V_{kJ}(R)$ only represents the *potential* energy of the motion of the nuclei. 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. 166) 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 oscillations represents not only 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 glue (electronic cloud), Fig. 6.1.

If we were interested in the motion of the *balls*, we 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 way the glue’s elastic energy depends on the stretching or squeezing of the glue 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 glue (electronic energy).¹⁷

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 of the gum into account. This effect is analogous to the second term in eq. (6.25) for $V_{kJ}(R)$.

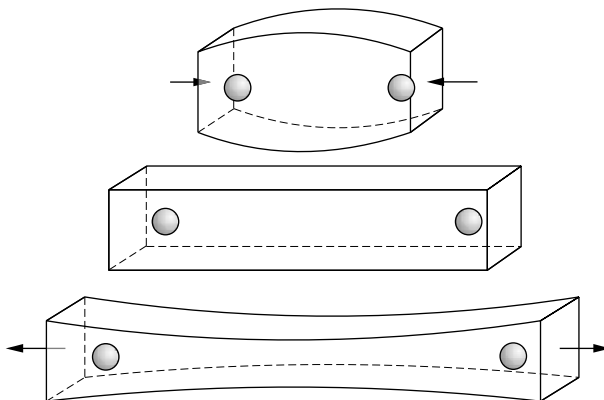


Fig. 6.1. Two metallic balls in a block of transparent glue. How they will vibrate? This will be dictated by the elastic properties of the glue.

¹⁷The 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 (1967) 116. The authors selected a slow intermolecular motion proceeding in the potential energy averaged over fast intramolecular motions.

6.5.2 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 $V_{kJ}(\mathbf{R})$ therefore represents a surface in $(3N - 5)$ -dimensional space (a *hypersurface*). This potential energy (hyper)surface $V_{kJ}(\mathbf{R})$, 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 a molecule.*

potential energy
surface (PES)

It is only because of the adiabatic approximation, that we may imagine the 3D shape of a molecule as a configuration of its nuclei (corresponding to a minimum of the electronic energy) bound by an electronic cloud, Fig. 6.2. This object moves and rotates in space, and in addition, the nuclei vibrate about their equilibrium positions with respect to other nuclei.

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

- the molecule does not have any particular 3D shape,
- the motion of the electrons and nuclei are 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, we should expect more help from theory.

For the benzene molecule, we could answer the questions like: what is the mean value of the carbon–carbon, carbon–proton, proton–proton, electron–electron, electron–proton, electron–carbon distances in its ground and excited state. Note that because all identical particles are indistinguishable, for example, 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 (non-relativistic though) 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 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 towards much more fertile regions.

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

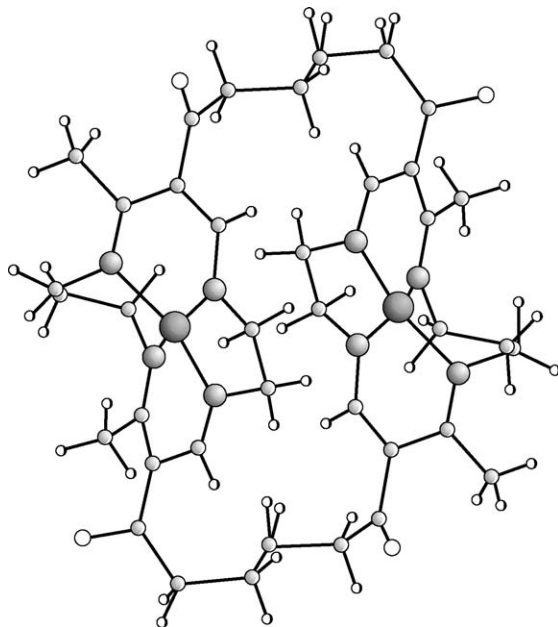


Fig. 6.2. A 3D *model* (called the “structure”) of a molecule allows us to focus attention on spatial and temporal relations that are *similar* to those we know from the macroscopic world. Although the concept of “spatial structure” may occasionally fail, in virtually all cases in chemistry and physics we use a 3D molecular model which resembles what is shown in the figure for a particular molecule (using a 2D projection of the 3D model). There are “balls” and “connecting sticks”. The balls represent atoms (of various sizes, 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 not? First, the scale. The real molecule is about 100 000 000 times smaller than the picture in the figure. Second, the motion. This static model shows a kind of averaging over all the snapshots of the real oscillating 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 in the figure has two tetraazaanulene macrocycles that coordinate two Ni^{2+} ions (the largest spheres). The macrocycles are held together by two $-(\text{CH}_2)_4-$ molecular links. Note that any atom of a given type binds a certain number of its neighbours. The most important message is: *if such structural information offered by the 3D 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.

In the chapters to come, 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.¹⁸ 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.

¹⁸Sometimes too much. We always have to remember that the useful model represents nothing more than a kind of better or worse pictorial representation of a more complex and unknown reality.

6.6 BASIC PRINCIPLES OF ELECTRONIC, VIBRATIONAL AND ROTATIONAL SPECTROSCOPY

6.6.1 VIBRATIONAL STRUCTURE

Eq. (6.24) represents the basis of molecular spectroscopy, and involves changing the molecular electronic, vibrational or rotational state of a diatomic molecule. Fig. 6.3 shows an example how the curves $U_k(R)$ may appear for three electronic states $k = 0, 1, 2$ of a diatomic molecule. Two of these curves ($k = 0, 2$) have a typical “hook-like” shape for bonding states, the third ($k = 1$) is also typical, but for repulsive electronic states.

It was assumed in Fig. 6.3 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 χ_{kvJ} was found: $\chi_{000}, \chi_{010}, \chi_{020}, \dots$ with energies $E_{000}, E_{010}, E_{020}, \dots$, respectively. Then, in a similar way, for $k = 2$, one has obtained the series of solutions: $\chi_{200}, \chi_{210}, \chi_{220}, \dots$ with the corresponding energies $E_{200}, E_{210}, E_{220}, \dots$. This means that these two electronic levels ($k = 0, 2$) have a *vibrational structure* ($v = 0, 1, 2, \dots$), the corresponding vibrational levels are shown in Fig. 6.3. Any attempt to find the vibrational levels for the electronic state $k = 1$ would fail (we will return to this problem later).

vibrational
structure

The pattern of the vibrational levels looks similar to those for the Morse oscillator (p. 173). The low levels are nearly equidistant, reminding us of the results

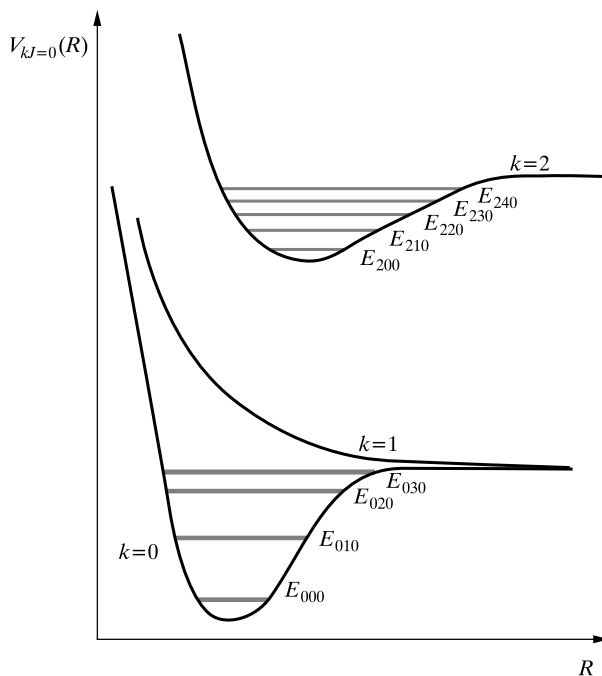


Fig. 6.3. The curves $V_{kJ}(R)$ for $J = 0$ [$V_{k0}(R) = U_k(R)$] for the electronic states $k = 0, 1, 2$ of a diatomic molecule (scheme). The vibrational energy levels E_{kvJ} for $J = 0$ corresponding to these curves are also shown. The electronic state $k = 0$ has four, $k = 1$ has zero, and $k = 2$ has five vibrational energy levels.

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 $V_{kJ}(R) = U_k(R) + J(J+1)\hbar^2/(2\mu R^2)$, in our case $V_{k1}(R) = U_k(R) + 1(1+1)\hbar^2/(2\mu R^2) = U_k(R) + \hbar^2/(\mu R^2)$ 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 . The potential energy curves just go up a little bit on the left.¹⁹ 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 upwards will result in a tiny shift upwards of all the computed vibrational levels. Therefore the levels E_{kv1} for $v = 0, 1, 2, \dots$ will be a little higher than the corresponding E_{kv0} for $v = 0, 1, 2, \dots$ (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 $J = 0, 1, 2, \dots$

rotational
structure

Increasing J means that the potential energy curve becomes shallower.²⁰ 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. At some lower J 's the molecule may accommodate all or part of the vibrational levels that exist for $J = 0$.

Example

Let us try this. An ideal experimental range for us would be a molecule with a Morse-like potential energy (p. 169), because here the problem is exactly solvable, yet preserves some important realistic features (e.g., dissociation). Unfortunately, even if we approximated $U_k(R) = E_k^0(R) + H'_{kk}(R)$ by a Morse curve, after adding the centrifugal term $J(J+1)\hbar^2/(2\mu R^2)$ the curve will no longer be of the

¹⁹With an accompanying small shift to the right the position of the minimum.

²⁰It is interesting to note that the force constant corresponding to the curves with $J \neq 0$ may, in principle, increase with respect to what we had for $J = 0$. At least this is what happens when approximating the $U_k(R)$ curve by a parabola (harmonic oscillator). Then, due to the curvature $6J(J+1)\frac{\hbar^2}{2\mu R^4}$ (always positive) of the term $J(J+1)\frac{\hbar^2}{2\mu R^2}$, we have an increase of the force constant due to rotational excitation. We have no information about whether this effect applies to more realistic potentials. For sufficiently high rotational excitations, when the minimum position of $V_{kJ}(R)$ is getting larger, the force constant has to converge to zero.

Morse type. However, what we would get, would certainly resemble a Morse potential. Indeed, the resulting curve approaches zero at $R \rightarrow \infty$ (as do all the Morse curves), and at the equilibrium point, R_e will be shifted up by $J(J+1)\hbar^2/(2\mu R_e^2)$, which we may ensure by taking a Morse curve with a little lower dissociation energy $D \rightarrow D' = D - J(J+1)\hbar^2/(2\mu R_e^2)$. As seen from Fig. 4.14, we should not worry too much about what to take as the parameter α , which controls the well width. Let us keep it constant. We could take any example we want, but since in Chapter 4 we used the Morse potential for the hydrogen bond between two water molecules, we have already a feeling for what happens there, so therefore let us stick to this example.

The Morse parameters we used were: $D = 6$ kcal/mol = 0.00956 a.u. = 2097 cm⁻¹, $\mu = 16560$ a.u. and $\alpha = 1$, and we have got 18 vibrational levels for two vibrating point-like water molecules. Then we computed (p. 175) $h\nu = 0.001074$ a.u. = 235 cm⁻¹. Let us try something special and take a very high rotational excitation²¹ $J = 40$. Let us calculate the new potential well depth D' assuming that $R_e = 5.6$ a.u., because this is what the hydrogen bond length amounts to. Then, we obtain $D' = 0.00798$ a.u., while $h\nu = 215$ cm⁻¹ a bit smaller in comparison with the state with no rotational excitation ($h\nu = 235$ cm⁻¹).

Now, let us turn to the problem of the number of energy levels. The new $a' = 16.257$, and therefore the possible values of b_v are: $b_0 = 15.757$, $b_1 = 14.757$, ..., so we have 16 allowed vibrational energy levels (and not 18 as we had before the rotational excitation). Two levels have vanished into thin air. We see that the molecule has been partially destabilized through rotational excitation. Higher excitations might result in dissociation.

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 later 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 absorption of UV or visible light, vibrational excitation to absorption of infrared radiation, and a rotational excitation, to absorption of microwave radiation.

UV-VIS,
IR spectra,
microwave
spectra

This is what we use in a microwave oven. Some chicken on a ceramic plate is irradiated by microwaves. This causes rotational excitation of the water molecules²² always present in food. The “rotating” water molecules cause a transfer of kinetic

²¹At small excitations the effect is less visible.

²²Such rotation is somewhat hindered in the solid phase.

energy to proteins, as would happen in traditional cooking. After removing the food from the microwave the chicken is hot, but the plate is cool (nothing to rotate in it).

In practice, our investigations always involve 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 centre-of-mass system, there will be allowed and forbidden energy intervals.²³ There is no energy levels in the forbidden intervals.²⁴ 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 $J = 0, 1, 2, \dots$. 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.

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, this makes the momentum of inertia $I = \mu R^2$ change and influences the rotation of the molecule²⁵ according to eq. (6.25), p. 231.

The separation is feasible only when making an approximation, e.g., when assuming the mean value of the momentum of inertia instead of the momentum 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 (6.25) for the oscillations in the form²⁶

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

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

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + U_k(R) \right) \chi_{kvJ}(R) = E' \chi_{kvJ}(R), \quad (6.26)$$

where the constant

$$E' = E_{kvJ} - E_{\text{rot}},$$

²³In a space-fixed coordinate system (see p. 971) we always have to do with a continuum of states (due to translations, see p. 61).

²⁴Corresponding to bound states. The non-bound states densely fill the total energy scale above the dissociation limit of the ground state.

²⁵Let us recall the energetic pirouette of charming dancer. Her graceful movements, stretching arms out or aligning them along the body, immediately translate into slow or fast rotational motion.

²⁶Which looks reasonable for *small* amplitude oscillations only.

$$E_{\text{rot}} = J(J+1) \frac{\hbar^2}{2\mu R_e^2}. \quad (6.27)$$

Now, we may always write the potential $U_k(R)$ as a *number* $U_k(R_e)$ plus the “rest” labelled by $V_{\text{osc}}(R)$:

rotational
energy

$$U_k(R) = U_k(R_e) + V_{\text{osc}}(R). \quad (6.28)$$

Then, it is appropriate to call $U_k(R_e)$ the *electronic energy* E_{el} (corresponding to the equilibrium internuclear distance in electronic state k), while the function $V_{\text{osc}}(R)$ stands, therefore, for the oscillation potential satisfying $V_{\text{osc}}(R_e) = 0$. After introducing this into eq. (6.26) we obtain the equation for oscillations (in general anharmonic)

electronic
energy

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{\text{osc}}(R) \right) \chi_{kvJ}(R) = E_{\text{osc}} \chi_{kvJ}(R),$$

where the *vibrational energy* $E_{\text{osc}} = E' - E_{\text{el}}$, hence (after adding the translational energy – recalling that we have separated the centre-of-mass motion) we have the final approximation

vibrational
energy

$$E_{kvJ} \approx E_{\text{trans}} + E_{\text{el}}(k) + E_{\text{osc}}(v) + E_{\text{rot}}(J), \quad (6.29)$$

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

A quasi-harmonic approximation

The detailed form of $V_{\text{osc}}(R)$ is obtained from $U_k(R)$ of eq. (6.28) and therefore from the solution of the Schrödinger equation (6.8) with the clamped nuclei Hamiltonian. In principle there is no other way but to solve eq. (6.26) 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 an 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 for shrinking*. It is true, that at the beginning, the spring may fulfil the harmonic law for shrinking too, but when $R \rightarrow 0_+$ 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 inconceivable. Fig. 6.4 shows the difference between the harmonic potential and the quasi-harmonic approximation for eq. (6.26).

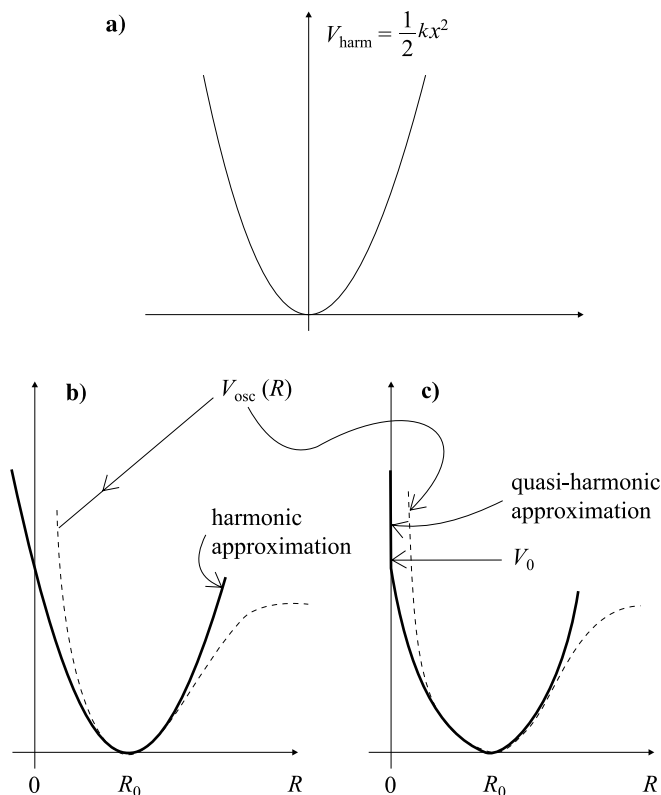


Fig. 6.4. The difference between harmonic and quasi-harmonic approximations for a diatomic molecule. (a) the potential energy for the harmonic oscillator (b) the harmonic approximation to the oscillator potential $V_{\text{osc}}(R)$ for a diatomic molecule is non-realistic, since at $R = 0$ (and at $R < 0$) the energy is finite, whereas it should go asymptotically to infinity when R tends to 0. (c) A more realistic (quasi-harmonic) approximation: 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 V_0 (high oscillation amplitudes), that practically it is of negligible importance. In cases (b) and (c), there is a range of small amplitudes where the harmonic approximation is applicable.

What do we do? Well, sticking to principles is always the best choice.²⁷ Yet, even in the case of the potential wall shown in Fig. 6.4c we have an analytical solution.²⁸ The solution is quite complex, but it gets much simpler assuming $\frac{V_0}{h\nu} \equiv \alpha \gg v$, where $v = 0, 1, 2, \dots$ stands for the vibrational quantum number we are

²⁷Let me stress once more that the problem appears when making the quasi-harmonic approximation, not in the real system we have.

²⁸E. Merzbacher, “*Quantum Mechanics*”, Wiley, New York, 2nd edition, 1970. The solution we are talking about has to be extracted from a more general problem in the reference above. 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 $R = 0$).

going to consider, and $V_0 \equiv V_{\text{osc}}(0)$. This means that we limit ourselves to those vibrational states that are much 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 $E_v = h\nu(v' + \frac{1}{2})$, where the modified “quantum number” $v' = v + \varepsilon_v$ with a tiny modification

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

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, $E_v = h\nu(v + \frac{1}{2})$, see Chapter 4.

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

6.8 POLYATOMIC MOLECULE

6.8.1 KINETIC ENERGY EXPRESSION

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

Let us consider a space fixed Cartesian coordinate system (SFCS, see Appendix I on p. 971), and vector \mathbf{R}_{CM} indicating the centre of mass of a molecule composed of M atoms, Fig. 6.5. Let us construct a Cartesian coordinate system (Body-Fixed Coordinate System, BFCS) with the origin in the centre of mass and the axes parallel to those of the SFCS (the third possibility in Appendix I).

In the BFCS an atom α of mass²⁹ M_α is indicated by the vector \mathbf{r}_α , and, its equilibrium position³⁰ by \mathbf{a}_α , the vector of displacement is $\boldsymbol{\xi}_\alpha = \mathbf{r}_\alpha - \mathbf{a}_\alpha$. If the molecule were *rigid and did not rotate* in the SFCS, then the velocity of the atom α would be equal to $\mathbf{V}_\alpha = \frac{d}{dt}(\mathbf{R}_{CM} + \mathbf{r}_\alpha) = \dot{\mathbf{R}}_{CM}$ (dots mean time derivatives), because the vector \mathbf{r}_α , indicating the atom from the BFCS, would not change at all. If, in addition, the molecule, still preserving its rigidity, is *rotated* about its centre of mass with angular velocity $\boldsymbol{\omega}$ (the vector having the direction of the rotation axis, right-handed screw orientation, and length equal to the angular velocity in radians per second), then the velocity of the atom α would equal³¹ $\mathbf{V}_\alpha = \dot{\mathbf{R}}_{CM} + (\boldsymbol{\omega} \times \mathbf{r}_\alpha)$. However, our molecule *is not rigid* and everything moves inside it (let us call these motions “vibrations”³²). Note that *no restriction was made with respect to the*

²⁹What this mass really means is still a unsolved problem. The essence of the problem is what electrons do when nuclei move. Besides the kinetic energy of the nuclei, we have to add the kinetic energy of the electrons that move together with the nuclei. We will leave this problem unsolved and treat M_α as the mass of the corresponding *atom*.

³⁰We assume that such a position exists. If there are several equilibrium positions, we just choose one of them.

³¹ $|\boldsymbol{\omega} \times \mathbf{r}_\alpha| = \omega r_\alpha \sin \theta$, where θ stands for the angle axis/vector \mathbf{r}_α . 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 $r_\alpha \sin \theta$.

³²Such a “vibration” may mean an oscillation of the OH bond, but also a rotation of the $-\text{CH}_3$ group or a large displacement of a molecular fragment.

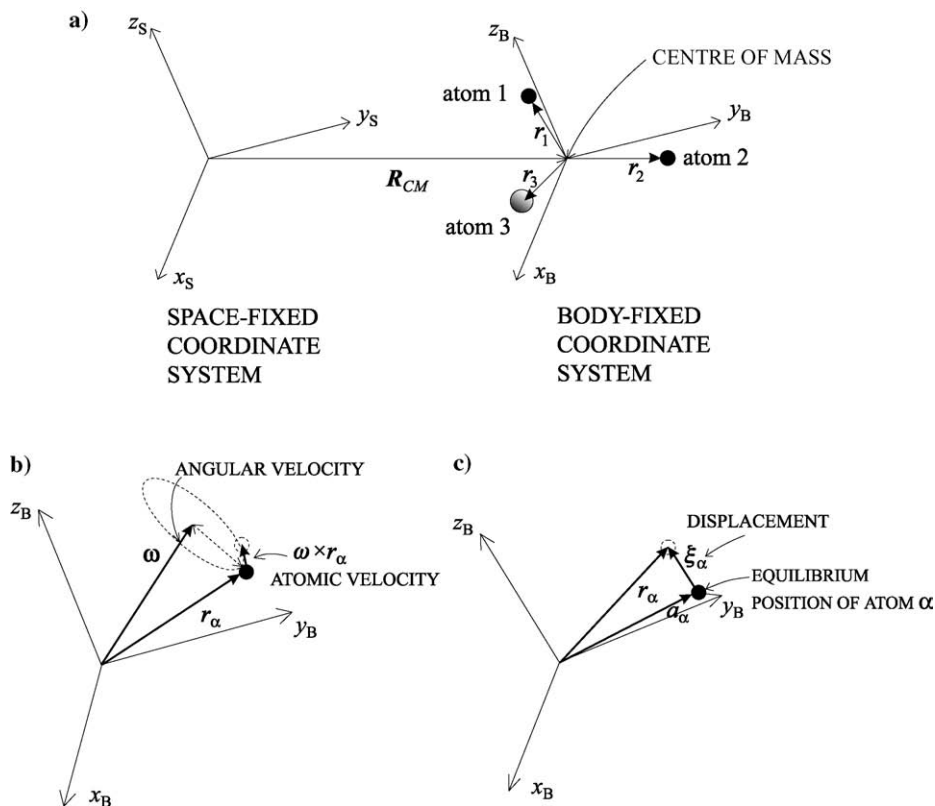


Fig. 6.5. Space- and Body-Fixed Coordinate Systems (SFCS and BFCS). (a) SFCS is a Cartesian coordinate system arbitrarily chosen in space (left). The origin of the BFCS is located in the centre of mass of the molecule (right). The centre of mass is shown by the vector R_{CM} from the SFCS. The nuclei of the atoms are indicated by vectors $r_1, r_2, r_3 \dots$ from the BFCS. Fig. (b) shows what happens to the velocity of atom α , when the system is rotating with the angular velocity given as vector ω . In such a case the atom acquires additional velocity $\omega \times r_\alpha$. Fig. (c) shows that if the molecule vibrates, then atomic positions r_α differ from the equilibrium positions a_α by the displacements ξ_α .

displacements ξ_α – there could be some giant internal motions. Then, the velocity of the atom α with respect to the SFCS is

$$V_\alpha = \dot{R}_{CM} + (\omega \times r_\alpha) + \dot{\xi}_\alpha. \quad (6.30)$$

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

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

The first three (“diagonal”) terms have a clear interpretation. These are: the kinetic energy of the centre of mass, the kinetic energy of rotation, and the kinetic energy of vibrations. The three further terms (“non-diagonal”) denote the *roto-translational*, *vibro-translational* and *vibro-rotational* couplings.

6.8.2 SIMPLIFYING USING 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 (\mathbf{R}_{CM}), three that determine rotation ($\boldsymbol{\omega}$) and on top of that M vectors \mathbf{r}_α . Too many. Six are redundant. Using such coordinates would be very annoying, because we have to take into account that they are non-independent.³³

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

$$\sum_{\alpha} M_{\alpha} \mathbf{r}_{\alpha} = \mathbf{0}, \quad (6.31)$$

also true when the atoms occupy equilibrium positions

$$\sum_{\alpha} M_{\alpha} \mathbf{a}_{\alpha} = \mathbf{0}.$$

Hence, we obtain a useful relation

$$\begin{aligned} \sum_{\alpha} M_{\alpha} (\mathbf{r}_{\alpha} - \mathbf{a}_{\alpha}) &= \mathbf{0}, \\ \sum_{\alpha} M_{\alpha} \boldsymbol{\xi}_{\alpha} &= \mathbf{0}, \end{aligned}$$

which, after differentiation with respect to time, becomes first Eckart condition

$$\sum_{\alpha} M_{\alpha} \dot{\boldsymbol{\xi}}_{\alpha} = \mathbf{0}. \quad (6.32)$$

first Eckart
condition

Inserting (6.31) and (6.32) into the kinetic energy expression makes the *roto-translational* and *vibro-translational* couplings vanish. Thus, we have

$$\begin{aligned} T &= \frac{1}{2} (\dot{\mathbf{R}}_{CM})^2 \sum_{\alpha} M_{\alpha} + \frac{1}{2} \sum_{\alpha} M_{\alpha} (\boldsymbol{\omega} \times \mathbf{r}_{\alpha})^2 + \frac{1}{2} \sum_{\alpha} M_{\alpha} (\dot{\boldsymbol{\xi}}_{\alpha})^2 \\ &\quad + \sum_{\alpha} M_{\alpha} (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}) \cdot \dot{\boldsymbol{\xi}}_{\alpha}. \end{aligned}$$

Noting that $\mathbf{r}_{\alpha} = \mathbf{a}_{\alpha} + \boldsymbol{\xi}_{\alpha}$ and using the relation³⁴ $(\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C} = \mathbf{A} \cdot (\mathbf{B} \times \mathbf{C})$, we obtain immediately

$$\begin{aligned} T &= \frac{1}{2} (\dot{\mathbf{R}}_{CM})^2 \sum_{\alpha} M_{\alpha} + \frac{1}{2} \sum_{\alpha} M_{\alpha} (\boldsymbol{\omega} \times \mathbf{r}_{\alpha})^2 + \frac{1}{2} \sum_{\alpha} M_{\alpha} (\dot{\boldsymbol{\xi}}_{\alpha})^2 \\ &\quad + \boldsymbol{\omega} \cdot \sum_{\alpha} M_{\alpha} (\mathbf{a}_{\alpha} \times \dot{\boldsymbol{\xi}}_{\alpha}) + \boldsymbol{\omega} \cdot \sum_{\alpha} M_{\alpha} (\boldsymbol{\xi}_{\alpha} \times \dot{\boldsymbol{\xi}}_{\alpha}). \end{aligned}$$

³³And we would have to check all the time, whether their values are consistent.

³⁴These are two ways of calculating the volume of the parallelepiped according to the formula: surface of the base times the height.

second Eckart
condition

We completely get rid of the redundancy if the second *Eckart condition*³⁵ is imposed (equivalent to three conditions for the coordinates)

$$\sum_{\alpha} M_{\alpha}(\mathbf{a}_{\alpha} \times \dot{\xi}_{\alpha}) = \mathbf{0}. \quad (6.33)$$

The condition means that *we do not want the internal motion to generate any angular momentum*.³⁶ This completes our final expression for the kinetic energy of a polyatomic molecule

$$\begin{aligned} 2T = & (\dot{\mathbf{R}}_{CM})^2 \sum_{\alpha} M_{\alpha} + \sum_{\alpha} M_{\alpha}(\boldsymbol{\omega} \times \mathbf{r}_{\alpha})^2 + \sum_{\alpha} M_{\alpha}(\dot{\xi}_{\alpha})^2 \\ & + 2\boldsymbol{\omega} \cdot \sum_{\alpha} M_{\alpha}(\xi_{\alpha} \times \dot{\xi}_{\alpha}). \end{aligned} \quad (6.34)$$

The kinetic energy in a space-fixed coordinate system (SFCS) is composed of:

- the kinetic energy of the centre of mass,
- the rotational energy of the whole molecule,
- the kinetic energy of the internal motions (“vibrations”),
- the last term, usually very small, is known as the Coriolis term.³⁷ The term couples the internal motions (“vibrations”) within the molecule with its rotation.

6.8.3 APPROXIMATION: DECOUPLING OF ROTATION AND VIBRATIONS

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

Since the Coriolis term is small, in the first approximation we may decide to neglect it. Also, when assuming *small vibrational amplitudes* ξ_{α} , which is a reasonable approximation in most cases, we may replace \mathbf{r}_{α} by the corresponding equilibrium positions \mathbf{a}_{α} in the rotational term of eq. (6.34): $\sum_{\alpha} M_{\alpha}(\boldsymbol{\omega} \times \mathbf{r}_{\alpha})^2 \approx \sum_{\alpha} M_{\alpha}(\boldsymbol{\omega} \times \mathbf{a}_{\alpha})^2$, which is analogous to eq. (6.27). After these two approximations have been made the kinetic energy represents the sum of the three *independent*

³⁵Carl Eckart, professor at California Institute of Technology, contributed to the birth of quantum mechanics (e.g., C. Eckart, *Phys. Rev.* 28 (1926) 711).

³⁶The 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 (6.33), where one of these equilibrium positions is treated as a reference. *Assuming* (6.33) means that we restrict the molecular vibrations to have only small amplitudes about a single equilibrium position.

³⁷Gaspard Gustav de Coriolis (1792–1843), French engineer and mathematician, director of the Ecole Polytechnique in Paris. In 1829 Coriolis introduced the notion of work, the equivalence of work and energy, and also a coupling of rotation and vibrations.

terms (i.e. each depending on different variables)

$$T \cong \frac{1}{2} (\dot{\mathbf{R}}_{CM})^2 \sum_{\alpha} M_{\alpha} + \frac{1}{2} \sum_{\alpha} M_{\alpha} (\boldsymbol{\omega} \times \mathbf{a}_{\alpha})^2 + \frac{1}{2} \sum_{\alpha} M_{\alpha} (\dot{\boldsymbol{\xi}}_{\alpha})^2, \quad (6.35)$$

the translational kinetic energy of the centre of mass $\frac{1}{2} (\dot{\mathbf{R}}_{CM})^2 \sum_{\alpha} M_{\alpha}$, the rotational energy $\frac{1}{2} \sum_{\alpha} M_{\alpha} (\boldsymbol{\omega} \times \mathbf{a}_{\alpha})^2$ and the internal motion (“vibrational”) kinetic energy $\frac{1}{2} \sum_{\alpha} M_{\alpha} (\dot{\boldsymbol{\xi}}_{\alpha})^2$.

6.8.4 THE KINETIC ENERGY OPERATORS OF TRANSLATION, ROTATION AND VIBRATIONS

Eq. (6.35) may serve to construct the corresponding kinetic energy operator for a polyatomic molecule. There is no problem (see Chapter 1) with the translational term: $-\frac{\hbar^2}{2 \sum_{\alpha} M_{\alpha}} \Delta_{\mathbf{R}_{CM}}$, the vibrational term will be treated in Chapter 7, p. 294.

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

moment of
inertia

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

to be computed in the BFCS (see Appendix I on p. 971). The diagonalization of the matrix (Appendix K on p. 982) corresponds to a certain rotation of the BFCS to a coordinate system *rotating with the molecule* (RMCS), and gives as the eigenvalues³⁸ I_{xx} , I_{yy} , I_{zz} . Then the classical expression for the kinetic energy of rotation takes the form³⁹

spherical,
symmetric,
asymmetric tops

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

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

³⁸If $I_{xx} = I_{yy} = I_{zz}$, the body is called a spherical top (example: methane molecule); if $I_{xx} = I_{yy} \neq I_{zz}$, it is called a symmetric top (examples: benzene, ammonia molecules); if $I_{xx} \neq I_{yy} \neq I_{zz}$, then the top is asymmetric (example: water molecule).

³⁹H. Goldstein, “Classical Mechanics”, 2nd edition, Addison-Wesley, 1980.

ity. Therefore, the middle part of the above formula for kinetic energy represents an analogue of $\frac{mv^2}{2}$ and the last part is an analogue of $\frac{p^2}{2m}$.

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 RMCS⁴⁰), whereas the quantum mechanical operators were introduced (Chapter 1) only for the Cartesian coordinates (p. 19). How do we write an operator expressed in some curvilinear coordinates q_i and the corresponding momenta p_i ? Boris Podolsky solved this problem⁴¹ and the result is:

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

metric tensor

where $\hat{p}_i = -i\hbar \frac{\partial}{\partial q_i}$, \mathbf{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 $g = \det \mathbf{G}$ and g_{rs} being in general some functions of q_r .

6.8.5 SEPARATION OF TRANSLATIONAL, ROTATIONAL AND VIBRATIONAL MOTIONS

Eq. (6.35) represents approximate kinetic energy. To obtain the corresponding Hamiltonian we have to add the potential energy for the motion of the nuclei, U_k , to this energy where k labels the electronic state. The last energy depends uniquely on the variables ξ_α that describe atomic vibrations and corresponds to the electronic energy $U_k(R)$ of eq. (6.28), except that instead of the variable R , which pertains to the oscillation, we have the components of the vectors ξ_α . Then, in full analogy with (6.28), we may write

$$U_k(\xi_1, \xi_2, \dots, \xi_N) = U_k(\mathbf{0}, \mathbf{0}, \dots, \mathbf{0}) + V_{k,\text{osc}}(\xi_1, \xi_2, \dots, \xi_N),$$

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

Since (after the approximations have been 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. (6.29))

$$E \approx E_{\text{trans}} + E_{\text{el}}(k) + E_{\text{rot}}(J) + E_{\text{osc}}(v_1, v_2, \dots, v_{3N-6}). \quad (6.36)$$

⁴⁰The rotation is carried out by performing three successive rotations by what is known as Euler angles. For details see Fig. 14.3, also R.N. Zare, “*Angular Momentum*”, Wiley, New York, 1988, p. 78.

⁴¹B. Podolsky, *Phys. Rev.* 32 (1928) 812.

6.9 NON-BOUND STATES

Repulsive potential

If we try to solve eq. (6.26) for oscillations 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 the eigenfunctions and the corresponding eigenvalues would form a continuum. These eigenvalues usually reflect the simple fact that the system has dissociated and its dissociation products may have any kinetic energy larger than the dissociation limit (i.e. having dissociated fragments with no kinetic energy), all energies measured in SFCs. 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 a corresponding total energy E , and that the system is allowed to relax according to the potential energy shown in Fig. 6.6.a. The system slides down the potential energy curve (the potential energy lowers) and, since the total energy is conserved its kinetic energy increases accordingly. Finally, the potential energy

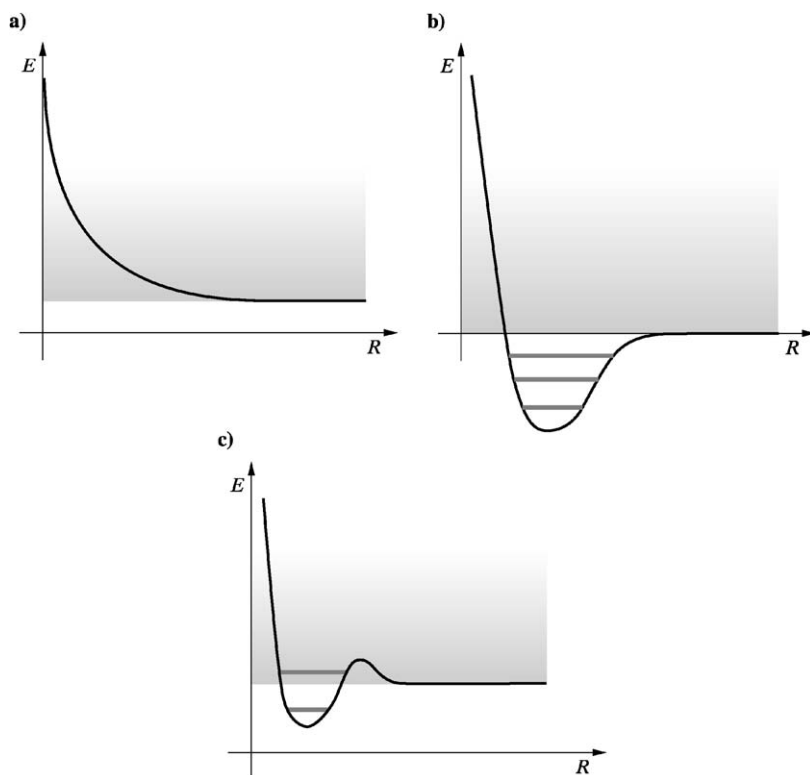


Fig. 6.6. Three different electronic states (R is the internuclear distance): (a) repulsive state (no vibrational states), (b) three bound (vibrational) states, (c) one bound vibrational state and one metastable vibrational state. A continuum of allowed states (shadowed area) is above the dissociation limit.

curve flattens, attaining $E_A + E_B$, where E_A denotes the internal energy of the fragment A (similarly for B). The final kinetic energy is equal to $E - (E_A + E_B)$ in SFCS.

“Hook-like” curves

Another typical potential energy curve is shown in Fig. 6.6.b, and has the shape of a hook. Solving (6.26) for such a curve usually⁴² gives a series of bound states, i.e. with their wave functions (Fig. 6.7) concentrated in a finite region of space and exponentially vanishing on leaving it. Fig. 6.6 shows the three discrete energy levels found, and the continuum of states above the dissociation limit, similar to the curve in Fig. 6.6.a. 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).

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. 6.6.c). The continuum extends upward the dissociation limit irrespectively of what kind of potential energy curve one has for finite

density of states

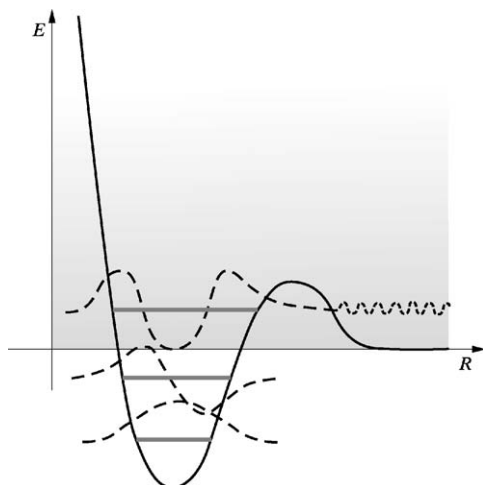


Fig. 6.7. The bound, continuum and resonance (metastable) states of an anharmonic oscillator. Two discrete bound states are shown (energy levels and wave functions) in the lower part of the figure. The continuum (shaded area) extends above the dissociation limit, i.e. the system may have any of the energies 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-hand side. They indicate that the function is non-normalizable and that the system will sooner or later dissociate.

⁴²For a sufficiently deep and large potential energy well.

values of R . In cases similar to that of Fig. 6.6.c the continuum will exist independently of how large and high the barrier is. But, the barrier may be so large that the system will have no idea about any “extra-barrier life”, and therefore will have its “quasi-discrete” states with the energy higher than the dissociation limit. Yet, these states despite its similarity to bound states belong to the continuum (are non-normalizable). Such states are metastable and are called *resonances* (cf. p. 159), 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. 6.7 shows how the metastable and stationary states differ: the metastable ones do not vanish in infinity.

resonances
encounter
complex

As shown in Fig. 6.8 rotational excitations may lead to a qualitative change of the potential energy curve for the motion of the nuclei. Rotational excitations lower the dissociation energy of the molecule. They may also create metastable vibrational states (vibrational resonances).

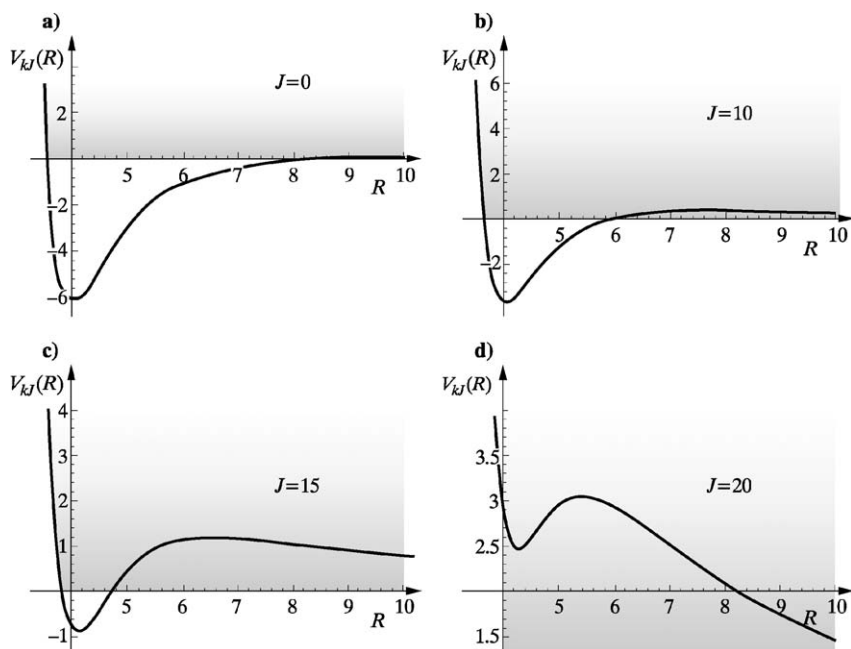


Fig. 6.8. Rotational excitation may lead to creating the resonance states. As an illustration a potential energy curve $V_{kJ}(R)$ of eq. (6.24) has been chosen that resembles what we would have for two water molecules bound by the hydrogen bond. Its first component $U_k(R)$ is taken in the form of the so called Lennard-Jones potential (cf. p. 287) $U_k(R) = \varepsilon_k [(\frac{R_{ek}}{R})^{12} - 2(\frac{R_{ek}}{R})^6]$ with the parameters for the electronic ground state ($k=0$): $\varepsilon_0 = 6$ kcal/mol and $R_{e0} = 4$ a.u. and the corresponding reduced mass $\mu = 16560$ a.u. For $J=0$ (a) the parameter ε_0 stands for the well depth, the R_{e0} denotes the position of the well minimum. Figs. (a), (b), (c), (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 the shallower the well: the rotation *weakens* the bond. Due to the centrifugal force a possibility of existence of the metastable resonance states appears. 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 that result from the fact that the dissociation products fly slower or faster, one may also have the continuum metastable or resonance states, that resemble the bound states.

The human mind wants to translate such situations into simple pictures, which help to “understand” what happens. Fig. 6.9 shows an analogy associated to astronomy: the Earth and the Moon are in a bound state, 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 the Space, then one has to

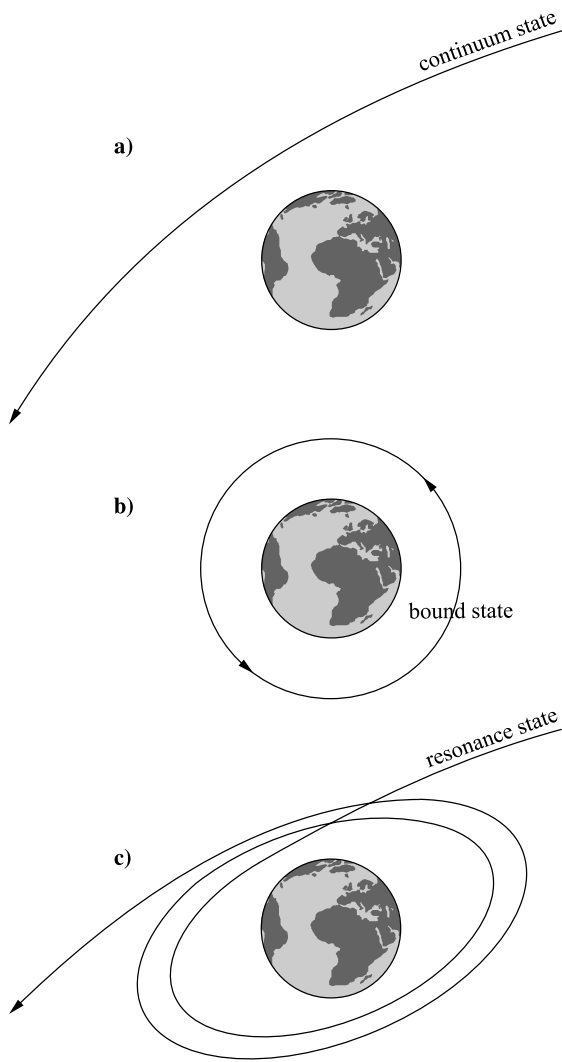


Fig. 6.9. Continuum, bound and resonance states – an analogy to the “states” of the Earth and an interacting body. (a) A “primitive” continuum state: an asteroid flies by the Earth and changes a little bit its trajectory. (b) A bound state: the Moon is orbiting around the Earth. (c) A resonance state: the asteroid was orbiting several times about the Earth and then flew away.

do with an analogue of a metastable or resonance state (characterized by a finite and non-zero life time).

The Schrödinger equation $\hat{H}\psi = E\psi$ is time-independent and, therefore, its solutions do not inform us about the sequence of events, but only all the possible events with their probability amplitudes. This is why the wave function for the metastable state of Fig. 6.7 exhibits oscillations at large x , it informs us about a possibility of dissociation.

Wave function “measurement”

Could we know a 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,⁴³ however, that the answer can also come from experiment. 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), see Fig. 6.10.

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

fluorescence

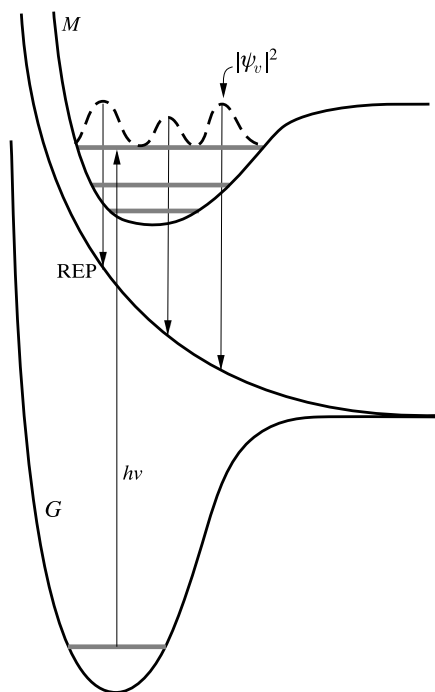


Fig. 6.10. A “measurement” of the wave function ψ_v , or more exactly of the corresponding probability density $|\psi_v|^2$. A molecule is excited from its electronic ground state G to a certain vibrational state ψ_v in the electronic excited state M . From M the molecule undergoes a fluorescence transition to the state REP . Since the REP state is of repulsive character the potential energy transforms into the kinetic energy (the total energy being preserved). By measuring the kinetic energy of the dissociation products one is able to calculate what their starting potential energy was, i.e. how high they were on the REP curve. This enables us to calculate $|\psi_v|^2$.

⁴³W. Koot, P.H.P. Post, W.J. van der Zande, J. Los, *Zeit. Physik D* 10 (1988) 233. The experimental data pertain to the hydrogen molecule.

James Franck (1882–1964), German physicist, professor at the Kaiser Wilhelm Institut für Physikalische Chemie in Berlin, then at the University of Göttingen, from 1935 at the John Hopkins University in the USA, and then at the University of Chicago. Franck 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 choose 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 obtained the Nobel Prize in 1925. The fact that, during the First World War, Franck was twice decorated with the Iron Cross was the reason that Franck was one of the few Jews whom the Nazis tolerated in academia.

Franck–Condon rule

have no time to move (*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.

Edward Condon, American physicist, one of the pioneers of quantum theory in the USA. In 1928 Condon and Gurney discovered the tunnelling effect. More widely known is his second great achievement – the Franck–Condon rule.



The kinetic energy of the dissociation products depends on the internuclear distance R when the fluorescence took place, i.e. on the length the system has to slide down the *REP*. How often such a R occurs depends on $|\psi_v(R)|^2$. Therefore, investigating the kinetic energy of the dissociation products gives $|\psi_v|^2$.

6.10 ADIABATIC, DIABATIC AND NON-ADIABATIC APPROACHES

Let us summarize the diabatic, adiabatic and non-adiabatic concepts, Fig. 6.11.

Adiabatic case. Suppose we have a Hamiltonian $\hat{H}(\mathbf{r}; \mathbf{R})$ that depends on the electronic coordinates \mathbf{r} and parametrically depends on the configuration of the nuclei \mathbf{R} . In practical applications, most often $\hat{H}(\mathbf{r}; \mathbf{R}) \equiv \hat{H}_0(\mathbf{r}; \mathbf{R})$, the electronic clamped nuclei Hamiltonian corresponding to eq. (6.8) (generalized to polyatomic molecules). The eigenfunctions $\psi(\mathbf{r}; \mathbf{R})$ and the eigenvalues $E_i(\mathbf{R})$ of the Hamiltonian $\hat{H}(\mathbf{r}; \mathbf{R})$ are called *adiabatic*, Fig. 6.11. If we take $\hat{H} = \hat{H}_0(\mathbf{r}; \mathbf{R})$, then in the adiabatic approximation (p. 227) the total wave function is represented by the

adiabatic states

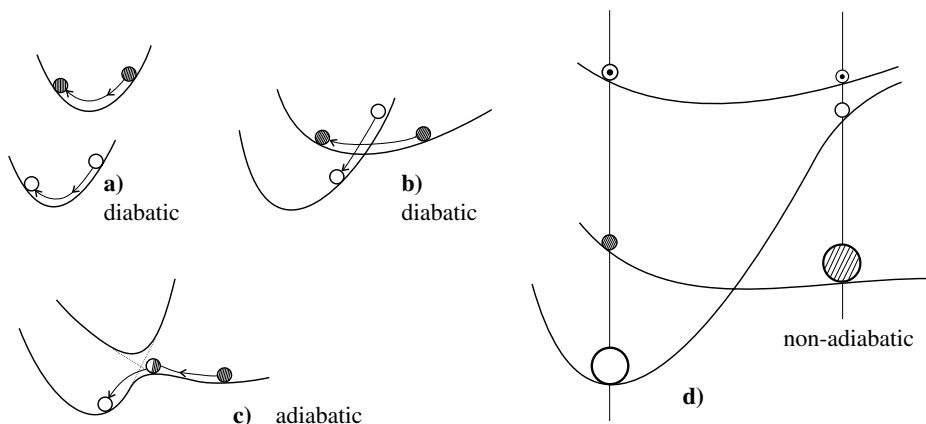


Fig. 6.11. The diabatic, adiabatic and non-adiabatic approaches to the motion of nuclei (a schematic view). (a) A state that preserves the chemical structure for any molecular geometry is called diabatic (e.g., is always ionic, or always covalent). The energies of these states are calculated as the mean values of the clamped nuclei Hamiltonian. In the lower-energy state, the system is represented by a white ball (say, the ionic state), in the second the system is represented by the black ball (say, covalent structure). These balls oscillate 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). Fig. (c) shows 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, eq. (6.8). 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 going through intermediate states shown as half-white and half-black ball). The total wave function is a product of the adiabatic electronic state and a rovibrational wave function. Finally, (d) pertains to 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, eq. (6.7). 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.

product

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}; \mathbf{R})f(\mathbf{R}), \quad (6.37)$$

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

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

diabatic states

$$\psi(\mathbf{r}; \mathbf{R}) \approx \sum_i^M c_i \bar{\psi}_i(\mathbf{r}; \mathbf{R}). \quad (6.38)$$

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,⁴⁴ and from (6.38) we may recognize what kind of chemical structure dominates ψ . Thus, using the diabatic basis, there is a chance of an insight into the chemistry going on in the system.⁴⁵

The wave functions $\bar{\psi}_i$ are in general non-orthogonal (we assume them normalized). For each of them we may compute the mean value of the energy

$$\bar{E}_i(\mathbf{R}) = \langle \bar{\psi}_i | \hat{\mathcal{H}}(\mathbf{R}) | \bar{\psi}_i \rangle, \quad (6.39)$$

and we will call it the diabatic energy.

The key point is that we may compare the eigenvalues and eigenfunctions of $\hat{\mathcal{H}}(\mathbf{R})$, 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 \mathbf{R} , Fig. 6.11.a,b,c. These relations will be discussed in a minute.

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 \mathbf{R} . In a non-adiabatic approach the total wave function is a superposition of these product-like contributions [a generalization of eq. (6.7)]:

$$\Psi(\mathbf{r}; \mathbf{R}) \approx \sum_k \bar{\psi}_k(\mathbf{r}; \mathbf{R}) f_k(\mathbf{R}). \quad (6.40)$$

This sum means that in the non-adiabatic approach the motion of the system involves many potential energy surfaces at the same time, Fig. 6.11.d.

The diabatic and the adiabatic electronic states are simply two choices from 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 pat-

⁴⁴Let 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 $\text{Na}-\text{Cl}$. The adiabatic wave function $\psi(\mathbf{r}; \mathbf{R})$ 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.

⁴⁵Very 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. (6.38)). Such a definition leaves 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.

tern and the interplay among such patterns. The second basis set highlights the order of the eigenvalues of $\hat{\mathcal{H}}(\mathbf{R})$ (the lower/higher-energy adiabatic state).⁴⁶

6.11 CROSSING OF POTENTIAL ENERGY CURVES FOR DIATOMICS

6.11.1 THE NON-CROSSING RULE

Can the adiabatic curves cross when R changes?

To solve this problem in detail let us limit ourselves to the simplest situation: the two-state model (Appendix D). Let us consider a diatomic molecule and such an internuclear distance R_0 that the two electronic adiabatic states⁴⁷ $\psi_1(\mathbf{r}; R_0)$ and $\psi_2(\mathbf{r}; R_0)$ correspond to the non-degenerate (but close on the energy scale) eigenvalues of the clamped nuclei Hamiltonian $\hat{H}_0(R_0)$:

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

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

Now, we are interested in solving

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

for R in the vicinity of R_0 and ask, is it 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 :

$$\psi(\mathbf{r}; R) = c_1(R)\psi_1(\mathbf{r}; R_0) + c_2(R)\psi_2(\mathbf{r}; R_0). \quad (6.41)$$

Note that for this distance R

$$\hat{H}_0(R) = \hat{H}_0(R_0) + V(R), \quad (6.42)$$

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

$$E_{\pm}(R) = \frac{\bar{E}_1 + \bar{E}_2}{2} \pm \sqrt{\left(\frac{\bar{E}_1 - \bar{E}_2}{2}\right)^2 + |V_{12}|^2}, \quad (6.43)$$

⁴⁶In polyatomic systems there is a serious problem with the adiabatic basis (this is why the diabatic functions are preferred). As we will see later (p. 264), the adiabatic electronic wave function is multi-valued, and the corresponding rovibrational wave function, having to compensate for this (because the total wave function must be single-valued), also has to be multi-valued.

⁴⁷These 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).

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

$$\bar{E}_i(R) = \langle \psi_i(\mathbf{r}; R_0) | \hat{H}_0(R) | \psi_i(\mathbf{r}; R_0) \rangle = E_i(R_0) + V_{ii}(R). \quad (6.44)$$

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:

$$\bar{E}_1 - \bar{E}_2 = 0, \quad (6.45)$$

$$|V_{12}| = 0. \quad (6.46)$$

Two conditions, and a *single* changeable parameter R . If you adjust the parameter to fulfil 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

$$|H_{12}| \equiv \langle \psi_1 | \hat{H}_0(R) | \psi_2 \rangle = 0,$$

because $\hat{H}_0(R) = \hat{H}_0(R_0) + \hat{V}$, and $[(H_0(R_0))_{12}] = 0$ due to the orthogonality of both eigenfunctions of $\hat{H}_0(R_0)$.

Now we will refer to group theory (see Appendix C, p. 903). The Hamiltonian represents a fully symmetric object, whereas the wave functions ψ_1 and ψ_2 are not necessarily fully symmetrical, because they may belong to other irreducible representations of the symmetry group. Therefore, in order to make the integral $|H_{12}| = 0$, it is sufficient that ψ_1 and ψ_2 transform according to *different* irreducible representations (“have different symmetries”).⁴⁸ 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.

If two states of a diatomic molecule have *the same* symmetry, then the corresponding potential energy curves *cannot* cross.

⁴⁸ 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}_0 (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.

6.11.2 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:⁴⁹ $1s^2 2s^2 2p^6 3s^1$), 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 in the NaCl story the real film 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 wait a minute! There is a problem. Which 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 $I = 495.8 \text{ kJ/mol} = 0.1888 \text{ a.u.}$, whereas the electron affinity of chlorine is only $A = 349 \text{ kJ/mol} = 0.1329 \text{ a.u.}$ 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.⁵⁰ First, let us define the two diabatic states (the basis set) of the system: the $3s$ orbital of Na (when the electron resides on Na; we have atoms) denoted by $|3s\rangle$ and the $3p_z$ orbital of Cl (when the electron is on Cl; we have ions, z is the axis of the molecule) $|3p\rangle$. Now, what about the Hamiltonian $\hat{\mathcal{H}}$? Well, a reasonable model Hamiltonian may be taken as⁵¹

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

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

$$\bar{E}_1(R) \equiv \mathcal{H}_{11} = \langle 3s | \hat{\mathcal{H}} | 3s \rangle = -I - AS^2 - \frac{1}{R}S^2 + \exp(-R),$$

$$\bar{E}_2(R) \equiv \mathcal{H}_{22} = \langle 3p | \hat{\mathcal{H}} | 3p \rangle = -IS^2 - A - \frac{1}{R} + \exp(-R),$$

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

⁴⁹What these configurations really mean is explained in Chapter 8.

⁵⁰The other electrons in our approach will only influence the numerical values of the interaction parameters.

⁵¹ \mathbf{r} stands for the coordinates of the electron, for the diatomic molecule R replaces \mathbf{R} .

$\bar{E}_2(R) = -A$, when $R \rightarrow \infty$ (the electron binding energy by the sodium and by the chlorine atoms for dissociation into atoms and ions, respectively), which is already very important. The term $\exp(-R)$ mimics the repulsion of the inner shells of both atoms⁵² and guarantees that the energies go up (they should do) as $R \rightarrow 0$. 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:

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

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 $S = R \exp(-R/2)$. Why? Since $S = \langle 3s | 3p \rangle = 0$, if $R \rightarrow \infty$ or if $R \rightarrow 0$, and $S > 0$ for other values of R , then at least our formula takes care of this. In addition, Figs. 6.12.a,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 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), also quite close 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. (6.38). Appendix D (general case) gives the eigenvalues [$E_+(R)$ and $E_-(R)$] and the eigenfunctions (ψ_+ and ψ_-). Figs. 6.12.c,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 (Fig. 6.12.a, light gray) the energy does not change too much (flat energy curve), but if the ions do the same the energy goes down, because of Coulombic attraction (dark gray). Thus, the two adiabatic curves (that nearly coincide with the two diabatic curves, especially for large R) look as though they are going to cross each other (Figs. 6.12.a,b), but the two states have the same symmetry with respect to the molecular axis (note that $S \neq 0$) and, therefore, the crossing cannot occur, Fig. 6.12.d. As a result, the two curves avoid the crossing and, as shown in Fig. 6.12.c–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?

⁵²It prevents the two cores collapsing, cf. Chapter 13.

avoided
crossing

harpooning
effect

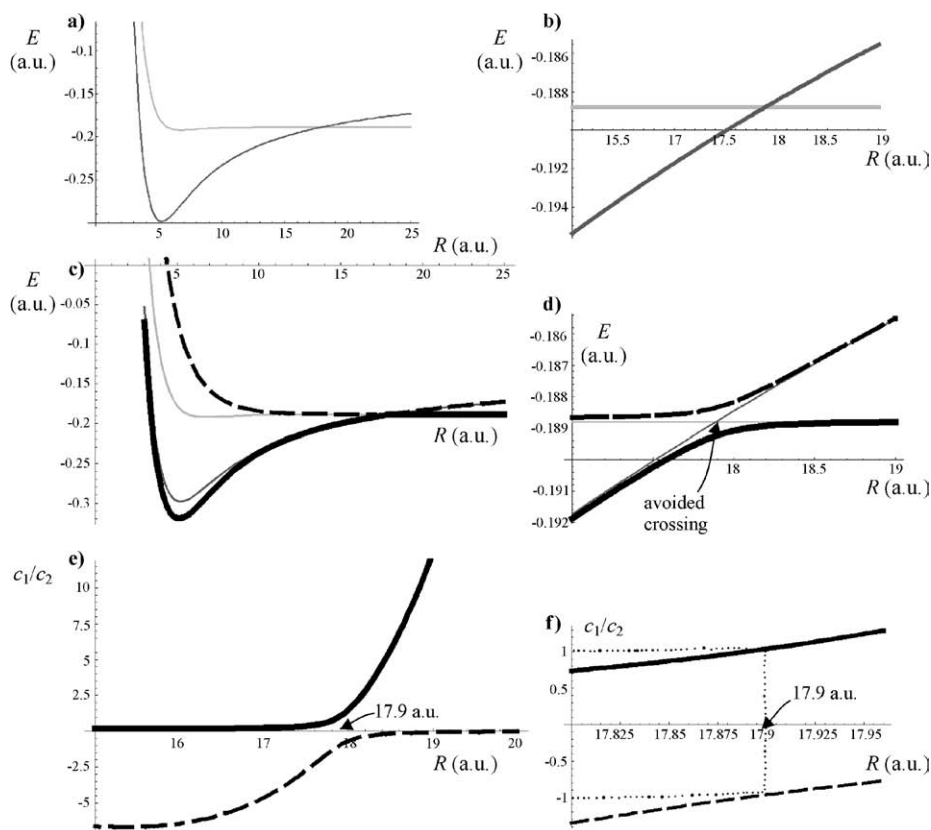


Fig. 6.12. A simple one-electron model of electron transfer in the NaCl molecule. R is the internuclear distance. (a) The mean values of the Hamiltonian with two *diabatic* states: one (light gray) being the $3s$ atomic orbital of the sodium atom (atomic curve), the second (dark gray) the $2p$ atomic 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 Fig. (d) (avoided crossing at 17.9 a.u.). (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 (dashed line) states, 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 . (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, 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 and the electron jump occurs. 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.

For large distances the adiabatic are practically identical with the diabatic states, except in the avoided crossing region, Figs. 6.12.c,d.

6.12 POLYATOMIC MOLECULES AND CONICAL INTERSECTION

Crossing for polyatomics

The non-crossing rule for a diatomic molecule has been based on eq. (6.43). To achieve the crossing we had to make two independent terms vanish with only one parameter (the internuclear distance R) able 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: $3N - 6$ in a molecule with N nuclei. For $N = 3$ one has already, therefore, 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.

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 $3N$ coordinates (\mathbf{O}_{3N})

All the quantities in eq. (6.43) depend on $n = 3N - 6$ 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 N point objects. To begin, let us construct a Cartesian system of $3N$ coordinates (\mathbf{O}_{3N}). Let us locate (Fig. 6.13) nucleus 1 at the origin (in this way we eliminate three degrees of freedom connected with the translation of the system), 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. This last possibility

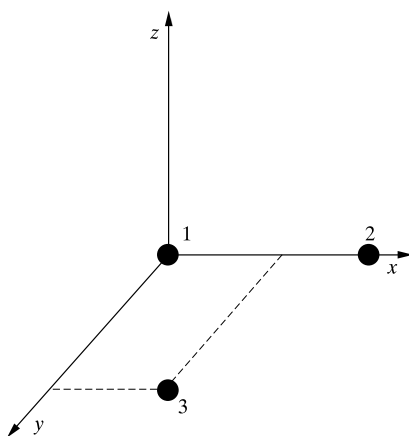


Fig. 6.13. The Cartesian coordinate system \mathbf{O}_{3N} and the atoms 1, 2, 3 with their fixed positions.

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 $3N$ coordinates. The other nuclei may be indicated by vectors (x_i, y_i, z_i) for $i = 4, 5, \dots, N$. As we can see there has been a lot of arbitrariness in these choices. By the way, if the molecule was diatomic, the third rotation need not be determined and the number of variables would be equal to $n = 3 \times 2 - 5 = 1$.

Cartesian system of $3N - 6$ coordinates (\mathbf{O}_{3N-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, y_3 and x_i, y_i, z_i for $i = 4, 5, \dots, N$. Thus, we have a Cartesian coordinate system (\mathbf{O}_{3N-6}) with $3 + 3(N - 3) = 3N - 6 = n$ axes, which may be labelled (in the sequence given above) in a uniform way: $\bar{x}_i, i = 1, 2, \dots, n$. A single point $\mathbf{R} = \bar{x}_1, \bar{x}_2, \dots, \bar{x}_{3N-6}$ in this n -dimensional space determines the positions of all N nuclei of the system. If necessary all these coordinates may be expressed by the old ones, but we are not intending to make this expression.

Two special vectors in the \mathbf{O}_{3N-6} space

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

$$\begin{aligned}\nabla(\bar{E}_1 - \bar{E}_2) &= \sum_{i=1}^{3N-6} \bar{i}_i \frac{\partial(\bar{E}_1 - \bar{E}_2)}{\partial \bar{x}_i}, \\ \nabla V_{12} &= \sum_{i=1}^{3N-6} \bar{i}_i \frac{\partial V_{12}}{\partial \bar{x}_i},\end{aligned}$$

where \bar{i}_i labels the unit vector along axis \bar{x}_i .

Rotating \mathbf{O}_{3N-6} to \mathbf{O}'_{3N-6}

We may introduce any coordinate system. We are free to do this because the system stays immobile, but our way of determining the nuclear coordinates changes. We will change the coordinate system in n -dimensional space once more. This new coordinate system is formed from the old one (\mathbf{O}_{3N-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 and \bar{x}_2) of the old coordinate system coincide with the plane determined by the two vectors: $\nabla(\bar{E}_1 - \bar{E}_2)$ or $\nabla(V_{12})$.

Let us denote the coordinates in the rotated coordinate system by $\xi_i, i = 1, 2, \dots, n$. The new coordinates can, of course, be expressed as some linear combinations of the old ones, but these details need not bother 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 $\nabla(\bar{E}_1 - \bar{E}_2)$ and ∇V_{12} . The directions $\nabla(\bar{E}_1 - \bar{E}_2)$ and ∇V_{12} need not be orthogonal, although they look this way in figures shown in the literature.⁵³

Now we are all set to define the conical intersection.

6.12.1 CONICAL INTERSECTION

Why has this, a slightly weird, coordinate system been chosen? We see from the formula (6.43) 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.⁵⁴

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

conical
intersection
subspace

Therefore, the hypersurface E_+ intersects with the hypersurface E_- , and their common part, i.e. the intersection set, are all those vectors of the n -dimensional space that fulfil 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.⁵⁵ When we withdraw from the point $(0, 0, \xi_3, \xi_4, \dots, \xi_{3N-6})$ 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. 6.14.a. For ξ_2 the situation is similar, but the cone may differ by its angle. From this it follows that

two diabatic hypersurfaces intersect with each other (the intersection set represents the subspace of all vectors $(0, 0, \xi_3, \xi_4, \dots, \xi_n)$) and split when we go out of the intersection point according to the *cone rule*, i.e. *linearly* when moving in the plane ξ_1, ξ_2 from the point $(0, 0)$.

⁵³See: F. Bernardi, M. Olivucci, M.A. Robb, *Chem. Soc. Rev.* (1996) 321. The authors confirmed to me that the angle is often quite small.

⁵⁴Let us take a scalar field V and calculate its value at the point $\mathbf{r}_0 + \mathbf{r}$, where we assume $|\mathbf{r}| \ll 1$. From the Taylor expansion we have with good accuracy, $V(\mathbf{r}_0 + \mathbf{r}) \cong V(\mathbf{r}_0) + (\nabla V)_{\mathbf{r}=\mathbf{r}_0} \cdot \mathbf{r} = V(\mathbf{r}_0) + |(\nabla V)_{\mathbf{r}=\mathbf{r}_0}| \cdot r \cos \theta$. We obtain the largest absolute value of the increment of V for $\theta = 0$ and $\theta = 180^\circ$, i.e. along the vector $(\nabla V)_{\mathbf{r}=\mathbf{r}_0}$.

⁵⁵If the axes ξ_1 and ξ_2 were chosen in another way *on the plane* determined by the vectors $\nabla(\bar{E}_1 - \bar{E}_2)$ 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* the energy would split into E_+ and E_- . Our choice stresses that the intersection of E_+ and E_- represents a $(n - 2)$ -dimensional subspace.

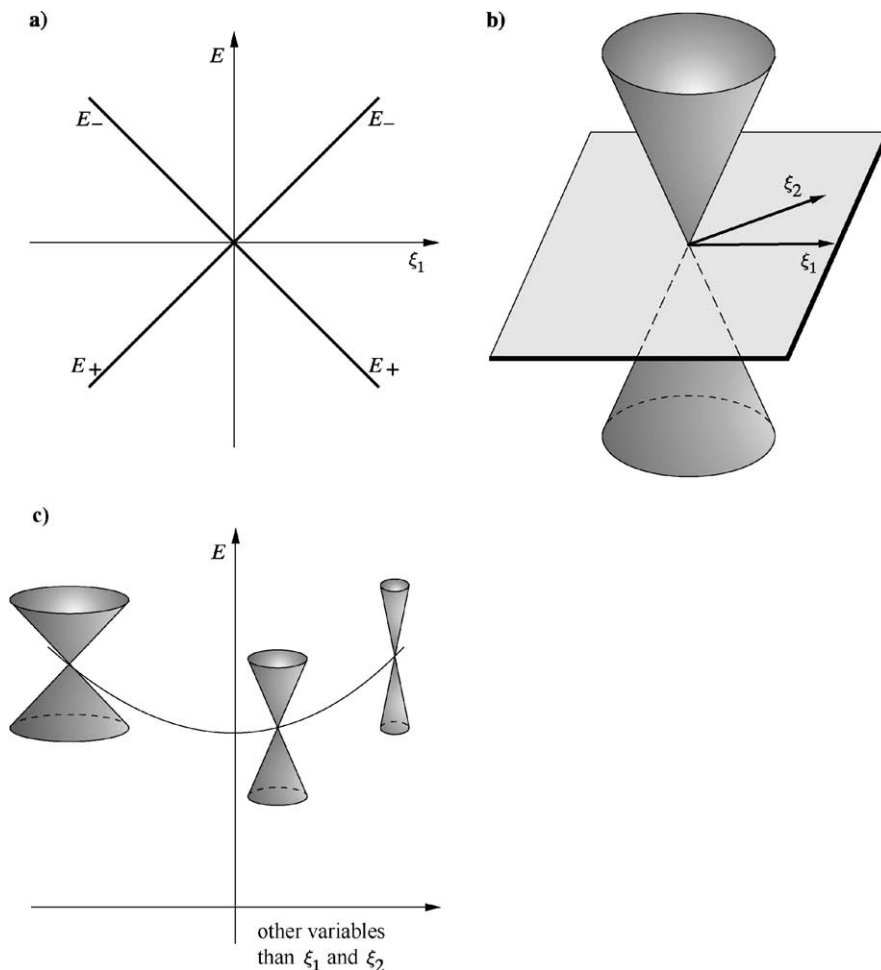


Fig. 6.14. Conical intersection: (a) a section of the cone along the ξ_1 axis; (b) the cone (variables ξ_1 and ξ_2); (c) the values of the other coordinates decide the cone opening angle as well as the intersection point energy.

This is called the *conical intersection*, Fig. 6.14.b. The cone opening angle is in general different for different values of the coordinates $\xi_3, \xi_4, \dots, \xi_{3N-6}$ see Fig. 6.14.c.

conical
intersection

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) adiabatic hypersurfaces are composed of two diabatic parts, which in polyatomics correspond to *different patterns of chemical bonds*. This means that the system, (point) when moving on the ground-state adiabatic hypersurface towards the join of the two parts, passes near the conical intersection point and overcomes the energy barrier. This is the essence of a chemical reaction.

6.12.2 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 formula (6.43): $\delta \equiv \frac{\bar{E}_1 - \bar{E}_2}{2}$, $h \equiv V_{12}$, and define α in the following way

$$\sin \alpha = \delta/\rho, \quad \cos \alpha = h/\rho, \quad \text{where } \rho = \sqrt{\delta^2 + h^2}.$$

We will move around the conical intersection within the plane given by the vectors $\nabla\delta$ and ∇h . 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 assured by $\cos \alpha = h/\rho$. Similarly, we have a single maximum and a single minimum of $\nabla\delta$ (as must be when going around), when assuming $\sin \alpha = \delta/\rho$. We do not need more information about our itinerary because what we are interested in is 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 (6.43) and the corresponding coefficients of the diabatic states are reported in Appendix D (the first, most general case):

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

Thus,

$$\begin{aligned} \frac{c_{1,+}}{c_{2,+}} &= \frac{\sin \alpha + 1}{\cos \alpha} = \frac{(\sin \frac{\alpha}{2} + \cos \frac{\alpha}{2})^2}{\cos^2 \frac{\alpha}{2} - \sin^2 \frac{\alpha}{2}} = \frac{(\sin \frac{\alpha}{2} + \cos \frac{\alpha}{2})}{(\cos \frac{\alpha}{2} - \sin \frac{\alpha}{2})}, \\ \frac{c_{1,-}}{c_{2,-}} &= \frac{\sin \alpha - 1}{\cos \alpha} = \frac{-(\cos \frac{\alpha}{2} - \sin \frac{\alpha}{2})^2}{\cos^2 \frac{\alpha}{2} - \sin^2 \frac{\alpha}{2}} = -\frac{(\cos \frac{\alpha}{2} - \sin \frac{\alpha}{2})}{(\cos \frac{\alpha}{2} + \sin \frac{\alpha}{2})}. \end{aligned}$$

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

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

Now, let us make this journey by considering the wave functions ψ_+ and ψ_- at the angle α and at the angle $\alpha + 2\pi$. Note that $\cos \frac{\alpha+2\pi}{2} = \cos(\frac{\alpha}{2} + \pi) = -\cos \frac{\alpha}{2}$ and $\sin \frac{\alpha+2\pi}{2} = \sin(\frac{\alpha}{2} + \pi) = -\sin \frac{\alpha}{2}$. Therefore, both the electronic functions ψ_+ and ψ_- have to change their signs after the journey (“geometric” phase or Berry phase), i.e.

$$\psi_+(\alpha + 2\pi) = -\psi_+(\alpha) \quad \text{and} \quad \psi_-(\alpha + 2\pi) = -\psi_-(\alpha).$$

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 has to undergo a change of sign.

The role of the conical intersection – non-radiative transitions and photochemical reactions

The conical intersection was underestimated in the past. However, photochemistry demonstrated that it happens much more frequently than expected.

Laser light may excite a molecule from its ground to an excited electronic state (Fig. 6.15). Let us assume that the nuclei in the electronic ground state have their positions characterized by point P' in the configurational space (they vibrate in its neighbourhood, but let us ignore the quantum nature of these vibrations⁵⁶).

⁵⁶Electronic energy hypersurfaces represent the potential energy surface (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.

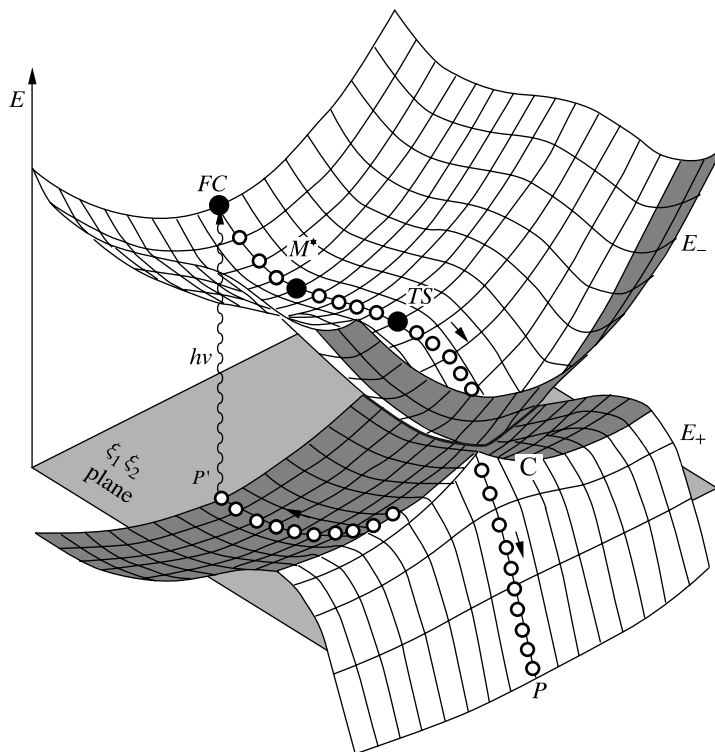


Fig. 6.15. The photochemical funnel effect. We can see two adiabatic surfaces (upper and lower), which resulted from intersection of two diabatic surfaces (white and gray). The lower surface corresponds to an electronic ground state, the upper to an excited electronic state. The molecule is excited from its ground state at the nuclear configuration P' to the excited state (point FC) at the same nuclear configuration (according to the Franck–Condon rule). The point FC representing the system is usually located on a slope of the potential energy (corresponding to the excited state) and this is why it slides downhill towards the energy minimum M^* . Its kinetic energy may be sufficient to go through M^* and pass a barrier (saddle point) corresponding to the point TS. Then, the system inevitably slides down into the conical intersection point C (“funnel effect”) and lands in the ground state surface (at the configuration of the conical intersection) with nearly 100% efficiency. The future of the system may correspond to different products: it may roll down to product P or slide back to product P' . Modified and adapted from F. Bernardi, M. Olivucci, M.A. Robb, *Chem. Soc. Rev.* (1996) 321.

The electronic excitation 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).

The point FC in Fig. 6.15 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 M^* in the excited state PES (E_-). In a few or a few tens of femtoseconds, the system slides down from P' to the

neighbourhood of M^* , transforming its potential energy into kinetic energy. Usually point M^* is separated from the conical intersection configuration C by a barrier with the corresponding potential energy saddle point TS (“transition state”). Behind the saddle point there is usually an energy valley⁵⁷ with a deep funnel ending in the conical intersection configuration. As soon as the system overcomes the barrier at TS, by going over it or by tunnelling, it will be sucked in by the conical intersection attractor with almost 100% probability.

funnel effect

The system goes through the “funnel” to the electronic ground-state hyper-surface.

Then the system will continue its path in the ground state PES, E_+ . If its momentum is large enough, the system slides down along path P towards the nearest local minimum. If its momentum is small, the system may choose path P' . The P trajectory may mean a new reaction product, while P' means returning to the original molecule.

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 neighbouring molecules (e.g., of the solvent).⁵⁸

energy
dissipation

What will the energy in the plane $\xi_1\xi_2$ be, far away from the conical intersection point? Of course, there is no reason for the energy to change linearly. Instead we may expect a more complex landscape to emerge on the E_+ and E_- PESs, such as minima, saddle points, etc. shown in Fig. 6.15. 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): to attach either to A or B

Thus any encounter of three atoms causes a conical intersection (see 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* like in an equilateral triangle configuration of H_3 . Similar “pivot points” may happen for four, five, six etc. atoms. Thus we will encounter not only the minima, maxima and saddle points, but also the conical intersection points when travelling 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

⁵⁷On the excited state PES.

⁵⁸The energy is usually distributed among the degrees of freedom in an unequal way.

corresponding permutational symmetry. All the details of PES will be repeated $N!$ times for a system with N identical nuclei. This will multiply the number of conical intersections.

More 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.

6.13 BEYOND THE ADIABATIC APPROXIMATION...

6.13.1 MUON CATALYZED NUCLEAR FUSION

Andrei Dmitrievich Sakharov (1921–1989) Russian physicist, 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 the 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 Sa-



kharov in 1945, in his first scientific paper, under the supervision of Tamm. In 1957 David Jackson realized that muons may serve as catalysts.

Some molecules look really peculiar, they may contain a muon instead of an electron. The muon is an unstable particle with the charge of an electron and mass equal to 207 electron masses.⁵⁹ For such a mass, assuming that nuclei are infinitely heavier than a 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 in 1960.⁶⁰ The idea behind the project was muon catalyzed fusion of deuterium and tritium. This fascinating problem was proposed by the Russian physicist Andrei Sakharov. Its essence is as follows.

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

The radius of the first Bohr orbit in the hydrogen atom (see p. 179) 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, instead an electron we have a muon, then μ would be equal about $250m$. 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, Fig. 6.16.a), and are able to overcome

muon catalysis

⁵⁹The muon was discovered in 1937 by C.D. Anderson and S.H. Neddermeyer. Its life time is about $2.2 \cdot 10^{-6}$ s. The muons belong to the leptons family (with the electron and τ particle, the later with mass equal to about 3640 electron masses). Nature created, for some unknown reasons, the “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?!”

⁶⁰W. Kołos, C.C.J. Roothaan, R.A. Sack, *Rev. Mod. Phys.* 32 (1960) 205.

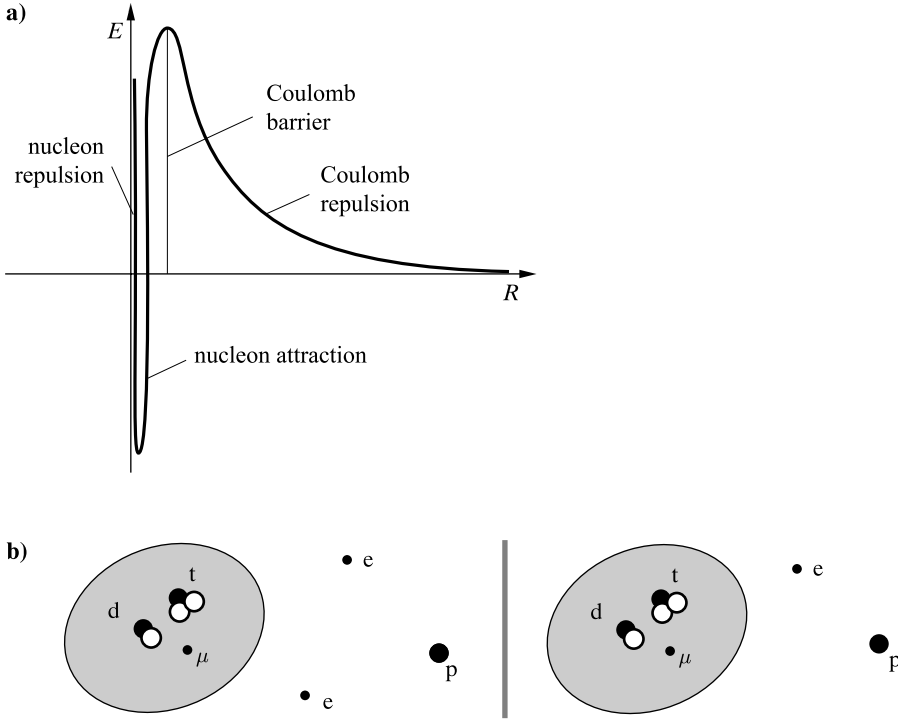


Fig. 6.16. (a) The interaction energy potential (E) of d and t as a function of the interparticle distance (R), with taking the nuclear forces into account (an outline). At large R , of the order of nanometers, we have Coulombic repulsion, at distances of the order of femtometers the internuclear attractive 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 analogues of H_2 and H_2^+ .

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.⁶¹ Everybody knows how much effort and money has been spent for decades (for the moment without success) to ignite the nuclear synthesis $d + t \rightarrow He$. 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.⁶²

⁶¹The commercial viability of this process will not be an option unless we can demonstrate 900 fusion events for each muon. About 10 grams of deuterium and 15 g of tritium fusion would then be sufficient to supply the average person with electricity for life.

⁶²More 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, X. Zhao, in “*Muon Catalyzed Fusion*”, eds. S.E. Jones, J. Rafelski, H.J. Monkhorst, AIP Conference Proceedings 181 (1989) 254.

6.13.2 “RUSSIAN DOLLS” – OR A MOLECULE WITHIN MOLECULE

Scrinzi and Szalewicz⁶³ carried out non-adiabatic calculations (p. 224) for a system of 6 particles: proton (p), deuterium (d), tritium (t), muon (μ) and two electrons (e) interacting by Coulombic forces (i.e. no nuclear forces assumed). It is not so easy to predict the structure of the system. It turns out that the resulting structure is a kind of “Russian doll”⁶⁴ (Fig. 6.16.b): the muon has acted according to its mass (see above) and created $td\mu$ with a dimension of about 0.02 \AA . 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 \AA . It turns out that the non-zero dimension of the “nucleus” makes a difference, and the energies computed with and without an approximation of the point-like 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 observe that the relaxation of the “nucleus” $dt\mu$ (from the excited state to the ground state⁶⁵) causes the ionization of the system: one of the electrons flies off. Such an effect 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 the nuclei. We will see this in Chapter 8, but even the $1s$ state of the hydrogen atom (p. 178, the maximum of the orbital is at the nucleus) 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 felt it was receiving much more freedom, so much that it could leave the molecule completely.

We may pose an interesting question, whether the “Russian doll” represents the global minimum of the particles system. We may imagine that the proton changes its position with the deuterium or tritium, i.e. new isomers (isotopomers⁶⁶) appear.

⁶³A. Scrinzi, K. Szalewicz, *Phys. Rev. A* 39 (1989) 4983.

⁶⁴((woman@ woman)@ woman)@)

⁶⁵A. Scrinzi, K. Szalewicz, *Phys. Rev. A* 39 (1989) 2855. The $dt\mu$ ion is created in the rovibrational state $J = 1$, $v = 1$, and then the system spontaneously goes to the lower energy 01 or 00 states. The energy excess causes one electron to leave the system (ionization). This is an analogue of the Auger effect in spectroscopy.

⁶⁶The 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

The authors did not study this question,⁶⁷ but investigated a substitution of the proton by deuterium and tritium (and obtained similar results).

Scrinzi and Szalewicz also performed some calculations for an analogue of H_2^+ : proton, deuterium, tritium, muon and electron. Here the “Russian doll” looks wonderful (Fig. 6.16.c); it is a four-level object:

- the molecular ion (the analogue 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).

Summary

- In the adiabatic approximation, the total wave function is approximated as a *product* $\Psi = \psi_k(\mathbf{r}; R)f_k(\mathbf{R})$ of the function $f_k(\mathbf{R})$, which describes the motion of the nuclei (vibrations and rotations) and the function $\psi_k(\mathbf{r}; R)$ that pertains to the motion of electrons (and depends parametrically on the configuration of the nuclei; here we give the formulae for a diatomic molecule). This approximation relies on the fact that the nuclei are thousands of times heavier than the electrons.
- The function $\psi_k(\mathbf{r}; R)$ represents an eigenfunction of the Hamiltonian $\hat{H}_0(R)$ of eq. (6.4), 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 function $f_k(\mathbf{R})$ is a *product* of a spherical harmonic⁶⁸ 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. 6.3 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 n , and the individual levels pertain to various vibrational and rotational states of the molecule in electronic state n ;
 - within the series for a given electronic state, there are groups of energy levels, each group characterized by a distinct vibrational quantum number ($v = 0, 1, 2, \dots$), and within the group the states of higher and higher energies correspond to the increasing rotational quantum number J ;
 - the energy levels fulfil some general relations:
 - * increasing n corresponds to an electronic excitation of the molecule (UV-VIS, *ultra-violet 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).

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.

⁶⁷They focused their attention on $\text{td}\mu$.

⁶⁸That is, of the eigenfunction for the rigid rotator.

- The electronic wave functions $\psi_k(\mathbf{r}; R)$ correspond to the energy eigenstates $E_k^0(R)$, which are functions of R . The energy curves⁶⁹ $E_k^0(R)$ for different electronic states k may cross each other, unless the molecule is diatomic and the two electronic states have the same symmetry.⁷⁰ In such a case we have what is known as an avoided crossing (see Fig. 6.12).
- For polyatomic molecules the energy hypersurfaces $E_k^0(\mathbf{R})$ can cross. The most important is *conical intersection* (Fig. 6.15) 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 and upper”). 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, *independence of the adiabatic hypersurface splitting of $3N - 8$ coordinates and dependence on two coordinates (ξ_1 and ξ_2) only*. The splitting begins by a linear dependence on ξ_1 and ξ_2 , which gives a sort of cone (hence the name “conical intersection”).
- 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 there is a mechanism for dissipation of the excess energy).

Main concepts, new terms

clamped nuclei Hamiltonian (p. 223)	diabatic curve (p. 253)
non-adiabatic theory (p. 224)	adiabatic curve (p. 253)
adiabatic approximation (p. 227)	avoided crossing (p. 255)
diagonal correction for the motion of the nuclei (p. 227)	non-crossing rule (p. 256)
Born–Oppenheimer approximation (p. 229)	harpooning effect (p. 257)
potential energy curve (p. 231)	conical intersection (p. 262)
potential energy (hyper)surface (p. 233)	Berry phase (p. 264)
electronic-vibrational-rotational spectroscopy (p. 235)	Franck–Condon rule (p. 266)
non-bound states (p. 247)	funnel effect (p. 266)
non-bound metastable states (p. 247)	non-radiative transitions (p. 266)
wave function “measurement” (p. 251)	photochemical reaction (p. 266)
	muon catalyzed nuclear fusion (p. 268)
	split nucleus effect (p. 270)

From the research front

Computing a reliable hypersurface of the potential energy (PES) for the motion of nuclei, represents an extremely difficult task for today’s computers, even for systems of four atoms. In principle routine calculations are currently performed for three-atomic (and, of course, two-atomic) systems. The technical possibilities are discussed by J. Hinze, A. Alijah and L. Wolniewicz, *Pol. J. Chem.* 72 (1998) 1293, in which the most accurate calculations are also reported (for the H_3^+ system). Analysis of conical intersections is only occasionally carried out, because the problem pertains to mostly unexplored electronic excited states.

⁶⁹As functions of R .

⁷⁰That is, they transform according to the same irreducible representation.

Ad futurum...

The computational effort needed to calculate the PES for an N atomic molecule is proportional to 10^{3N-6} . This strong dependence suggests that, for the next 20 years, it would be rather unrealistic to expect high-quality PES computations for $N > 10$. 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, because 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

J. Hinze, A. Alijah, L. Wolniewicz, "Understanding the Adiabatic Approximation; the Accurate Data of H_2 Transferred to H_3^+ ", *Pol. J. Chem.* 72 (1998) 1293.

The paper reports the derivation of the equation of motion for a *polyatomic* molecule. As the origin of the BFCS, unlike this chapter, the centre of mass was chosen.⁷¹

W. Kolos, "Adiabatic Approximation and its Accuracy", *Advan. Quantum Chem.* 5 (1970) 99.

Kolos was the No 1 expert in the domain.

F. Bernardi, M. Olivucci, M.A. Robb, "Potential Energy Surface Crossings in Organic Photochemistry", *Chem. Soc. Rev.* p. 321–328 (1996).

A review article by the top experts in conical intersection problems.

Questions

1. A diatomic homonuclear molecule, origin of the BFCS in the centre of the molecule, potential energy of the Coulombic interactions equals V . The total non-relativistic Hamiltonian is equal to:
 a) $\hat{H} = -\sum_i \frac{\hbar^2}{2m} \Delta_i - \frac{\hbar^2}{2\mu} \Delta_R$; b) $\hat{H} = -\sum_i \frac{\hbar^2}{2m} \Delta_i + V$; c) $\hat{H} = -\frac{\hbar^2}{2\mu} \Delta_R + V$; d) $\hat{H} = -\sum_i \frac{\hbar^2}{2m} \Delta_i + V - \frac{\hbar^2}{2\mu} \Delta_R - \frac{\hbar^2}{8\mu} (\sum_i \nabla_i)^2$.
2. A diatomic molecule, origin of the BFCS in the centre of the molecule. In the adiabatic approximation, the total wave function is in the form $\Psi = \psi_k(\mathbf{r}; R) f_k(\mathbf{R})$, where:
 a) $f_k(\mathbf{R})$ describes the translation of the molecule; b) $f_k(\mathbf{R})$ stands for a spherical harmonic describing the rotations of the molecule; c) $\psi_k(\mathbf{r}; R)$ denotes the eigenfunction of the clamped nuclei Hamiltonian; d) $\psi_k(\mathbf{r}; R)$ stands for the probability density of having the electrons with coordinates \mathbf{r} and the nuclei at distance R .
3. A diatomic molecule, origin of the BFCS in the centre of the molecule, in the adiabatic approximation the total wave function is in the form $\Psi = \psi_k(\mathbf{r}; R) f_k(\mathbf{R})$. The potential energy for the vibrations of the molecule is equal to:
 a) $V + J(J+1) \frac{\hbar^2}{2\mu R^2}$; b) $\langle \psi_k | \hat{H} \psi_k \rangle + (2J+1) \frac{\hbar^2}{2\mu R^2}$; c) $\langle \psi_k | \hat{H} \psi_k \rangle + J(J+1) \frac{\hbar^2}{2\mu}$; d) $\langle \psi_k | \hat{H} \psi_k \rangle + J(J+1) \frac{\hbar^2}{2\mu R^2}$.

⁷¹ We have chosen the centre of the ab bond.

4. The potential energy curves for the motion of the nuclei for a diatomic molecule
 - a) cross, if their derivatives differ widely; b) always cross; c) do not cross, if they correspond to the same irreducible representation of the symmetry group of the Hamiltonian; d) do not cross, if they correspond to different symmetry.
5. Please choose the *wrong* answer. The potential energy for the motion of the nuclei:
 - a) contains the eigenvalue of the clamped nuclei Hamiltonian;
 - b) does not change when the rotation excitation occurs;
 - c) represents the electronic energy when the Born–Oppenheimer approximation is used;
 - d) for bound states has to be convex as a function of the positions of the nuclei.
6. Please choose the *wrong* answer. As a result of the rotational excitation $J \rightarrow (J + 1)$ of a molecule of length R :
 - a) the angular momentum increases;
 - b) the potential for vibrations changes;
 - c) the potential energy curve for the motion of the nuclei becomes shallower;
 - d) the potential energy increases by a term proportional to $(2J + 1)$ and proportional to R^{-2} .
7. The potential energy hypersurface for the N -atomic molecule depends on the following number of variables:
 - a) $2N - 8$; b) $3N - 6$; c) $3N - 5$; d) N .
8. At the conical intersection (Born–Oppenheimer approximation), the cone angle:
 - a) does not depend on the direction of leaving the conical intersection point; b) is different for the lower and for the higher cones; c) depends on the values of coordinates other than those along directions $\nabla(\bar{E}_1 - \bar{E}_2)$ and $\nabla(V_{12})$; d) is different for different isotopomers.
9. At the conical intersection the following directions in configurational space lead to splitting between E_+ and E_- :
 - a) $\nabla(\bar{E}_1 - \bar{E}_2)$ and $\nabla(V_{12})$; b) $\nabla(\bar{E}_1)$ and $\nabla(\bar{E}_2)$; c) $\nabla(\bar{E}_1 \cdot \bar{E}_2)$ and $\nabla(V_{12})$; d) $\nabla(\bar{E}_1 + \bar{E}_2)$ and $\nabla(V_{12})$.
10. Please find the *wrong* answer. The adiabatic approximation:
 - a) is equivalent to the Born–Oppenheimer approximation; b) is related to the wave function in the form of a product of an electronic function and a function describing the motion of the nuclei; c) leads to the notion of the potential energy curve for the motion of the nuclei; d) is worse satisfied for molecules with muons instead of electrons.

Answers

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