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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

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ENERGY TRANSFER PROCESSES IN LASER ASSISTED COLLISIONS

A. BAMBINI

Istituto Elettronica Quantistica
C.N.R.
Firenze, Italy

Energy transfer processes in laser assisted collisions.

Lecture Notes

(Arturo Bambini)

Layout.

The Born Oppenheimer Approximation.

Molecular system. Description.

Electrostatic interaction (q representation)

$V_{nn}(Q)$ nucleus-nucleus
$V_{ne}(Q,q)$ nucleus-electron
$V_{ee}(q)$ electron-electron.

$\{Q\}$ nuclear coordinates $\{q\}$ electron coordinates.

Hamiltonian Operator

$$H = \hat{T}_n + \hat{T}_e + V_{nn} + V_{ne} + V_{ee}$$

$$\hat{T}_n = -\hbar^2 \sum_k \frac{\nabla_k^2}{2M_k}$$ M_k = mass of k-th nucleus

$$\hat{T}_e = -\frac{\hbar^2}{2m} \sum_l \nabla_l^2$$ m = electron mass.

$$V_{nn}(Q) + V_{ee}(q) + V_{ne}(Q,q) = \sum_{ij} \frac{Z_i Z_j e^2}{\rho_{ij}} + \sum_{kl} \frac{e^2}{r_{kl}} - \sum_{kj} \frac{Z_j e^2}{R_{kj}}$$

$\rho_{ij} = |\vec{Q}_i - \vec{Q}_j|$ i,j run over $1 \dots N_n$

$R_{kj} = |\vec{Q}_j - \vec{q}_k|$ k,l run over $1 \dots N_e$

$r_{kl} = |\vec{q}_k - \vec{q}_l|$ N_n, N_e number of nuclei and electrons respectively.

lecular Wavefunction (q representation) - Stationary state

$$\langle \vec{q},\vec{Q}|\Psi\rangle = \Psi(\vec{q},\vec{Q})$$

eying Schrödinger equation

$$H\psi = E\psi.$$

lectrons are much lighter than nuclei. Can we exploit this fact to ive $\psi(\vec{q},\vec{Q})$ a simpler structure?

e Born Oppenheimer assumption: the nuclei can be considered 'clamped' t fixed spatial positions for a sufficiently long time, so that electrons ach a stationary state for that nuclear (fixed) configuration.

lectronic wavefunction : $\phi(\vec{q},\vec{Q})$ where $\vec{Q}$ are just parameters. This is the configuration of the electrons when the nuclei are fixed at $\vec{Q}$.

Total wavefunction

$$\Psi(\vec{q},\vec{Q}) = \Phi(\vec{q},\vec{Q})\,\chi(\vec{Q}).$$

he $\hat{T}_n$ operator acts only on $\chi(\vec{Q})$, not on $\phi(\vec{q},\vec{Q})$. Hence

$$\chi(\vec{Q})\Big\{\big[\underbrace{V_{ne}(\vec{Q},\vec{q})+V_{ee}(\vec{q})+\hat{T}_e}_{H_e'(\vec{Q})}\big]\Phi(\vec{q},\vec{Q})\Big\} + \Phi(\vec{q},\vec{Q})\hat{T}_n\,\chi(\vec{Q}) + \Phi(\vec{q},\vec{Q})V_{nn}(\vec{Q})\chi(\vec{Q})$$

$$= E\,\phi\,\chi$$

here we have neglected terms containing $\nabla_Q^2\phi$ and $(\vec{\nabla}_Q\phi\cdot\vec{\nabla}_Q\chi)$.
Solving for

$$H_e'(\vec{Q})\,\Phi(\vec{q},\vec{Q}) = W(\vec{Q})\,\phi(\vec{q},\vec{Q}) \qquad (\vec{Q} = \text{constant})$$

and substituting back in the Schrödinger equation,

$$\big[\hat{T}_n + V_{nn}(\vec{Q}) + W(\vec{Q})\big]\chi(\vec{Q}) = E\chi(\vec{Q})$$

since

$$\int d\vec{q}\;\phi^*(\vec{q},\vec{Q})\,\phi(\vec{q},\vec{Q}) = 1 \qquad \text{for any } \vec{Q}.$$

This equation describes the nuclear motion in an effective potential $V_{nn}(\vec{Q}) + W(\vec{Q})$.

The general theory and the first adiabatic correction to the Born-Oppenheimer approximation.

The system is now described by a wavefunction that is a linear superposition of states

$$\Psi(\vec{q},\vec{Q}) = \sum_p \Phi_p(\vec{q},\vec{Q})\,\chi_p(\vec{Q})$$

The Schrödinger equation now is

$$\sum_p \big[\hat{T}_n + \hat{T}_e + V_{nn}(\vec{Q}) + V_{ne}(\vec{q},\vec{Q}) + V_{ee}(\vec{q})\big]\phi_p\chi_p = E\sum_p \phi_p\chi_p$$

and the wave equation for the nuclear motion becomes

$$\big[\hat{T}_n + \hat{V}_{nn}(\vec{Q}) + W_p(\vec{Q}) - E\big]\chi_p(\vec{Q}) + \sum_{\ell} c_{p\ell}\,\chi_\ell(\vec{Q}) = 0$$

where $c_{p\ell}$ are the operators

$$c_{p\ell} = \sum_{1}^{N_n}{}_k \;\frac{1}{M_k}\big(\vec{A}_{p\ell}^{(k)}\cdot\vec{P}_k + B_{p\ell}^{(k)}\big)$$

with

$$\vec{A}^{(k)}_{pl} = \int d\vec{q}\ \phi^*_p(\vec{q},\vec{Q})\ \vec{P}_k\ \Phi_l(\vec{q},\vec{Q})$$

$$B^{(k)}_{pl} = \frac{1}{2}\int d\vec{q}\ \phi^*_p(\vec{q},\vec{Q})\left[\vec{P}^2_k\ \Phi_l(\vec{q},\vec{Q})\right]$$

and

$$\vec{P}_k = -i\hbar\vec{\nabla}_{Q_k}.$$

The two terms $\nabla^2_Q\Phi$ and $(\vec{\nabla}_Q\Phi)\cdot(\vec{\nabla}_Q\chi)$ that were neglected in the Born-Oppenheimer approximation are now contained in the $B^{(k)}$ and $\vec{A}^{(k)}$ coefficients.

<u>Note</u> The diagonal coefficients c_{ll} are not operators, since

$$\vec{A}^{(k)}_{ll} = \int \Phi^*_l(\vec{q},\vec{Q})\vec{P}_k\ \phi_l(\vec{q},\vec{Q})\,d\vec{q} = \frac{1}{2}\int \vec{P}_k\ \left[\Phi_l(\vec{q},\vec{Q})\right]^2 d\vec{q}$$

[Φ_l can be taken real and $\vec{P}_k$ is a hermitian operator], and

$$\frac{1}{2}\int \vec{P}_k\ [\phi_l(\vec{q},\vec{Q})]^2\,d\vec{q} = \frac{1}{2}\vec{P}_k\int\phi^2_l(\vec{q},\vec{Q})\,d\vec{q} = 0$$

[Φ_l are normalized to 1 independently of $\vec{Q}$]. Hence

$$c_{ll} = \sum_{1}^{N_n}{}_k\ \frac{1}{M_k}\ B^{(k)}_{ll}.$$

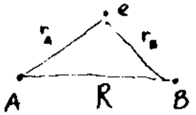
c_{ll} can then be added to $W_l(\vec{Q})$ to redefine the potential energy (effective potential energy):

$$V_{nn}(\vec{Q}) + W_l(\vec{Q}) \Rightarrow V_{nn}(\vec{Q}) + W_l(\vec{Q}) + c_{ll}(\vec{Q}).$$

c_{ll} is also called the adiabatic correction to the Born-Oppenheimer approximation.

<u>The LCAO method to build molecular wavefunctions $\phi(q,\vec{Q})$.</u>

The simplest molecular Hamiltonian is that for H_2^+



One electron in the Coulomb field of two nuclei at A and B.

$$H'_e = -\frac{\hbar^2\nabla^2}{2m} - \frac{Z_A e^2}{r_A} - \frac{Z_B e^2}{r_B} \qquad (\text{electronic})$$

$$H = H'_e + \frac{Z_A Z_B e^2}{R} - \frac{\hbar^2\nabla^2_A}{2M_A} - \frac{\hbar^2\nabla^2_B}{2M_B} \qquad (\text{total}).$$

This problem can be solved <u>exactly</u>. However we show here, instead of the exact solution, a method that can be generalized to more complicated systems.

<u>LCAO</u> (Linear Combination of Atomic Orbitals)

We start from the atomic wavefunctions φ_A and φ_B describin a single electron in the field of nuclei at A and B respectively. Then we write the molecular wavefunction ϕ as a linear superposition of φ_A and φ_B

$$\phi = c_A\varphi_A + c_B\varphi_B$$

and determine c_A, c_B so that the energy of the system at R = constant is a minimum:

$$E = \langle\phi|\,H'_e + \frac{Z_A Z_B}{R}\,|\phi\rangle \,/\, \langle\phi|\phi\rangle$$

minimum :

$$\frac{\partial E}{\partial c_A} = \frac{\partial E}{\partial c_B} = 0.$$

Note According to the Born-Oppenheimer assumption, we have disregarded the effects of ∇_A^2 and ∇_B^2 on ϕ.

Introducing the symbols

$$E_A = \langle \varphi_A | H'_e + \frac{Z_A Z_B}{R} | \varphi_A \rangle$$

$$E_B = \langle \varphi_B | H'_e + \frac{Z_A Z_B}{R} | \varphi_B \rangle$$

$$E_{AB} = \langle \varphi_A | H'_e + \frac{Z_A Z_B}{R} | \varphi_B \rangle$$

and the overlap integral

$$S = \langle \varphi_A | \varphi_B \rangle$$

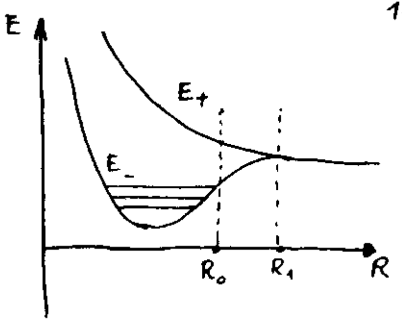
we obtain that E is a minimum if the algebraic equation

$$\begin{vmatrix} E_A - E & E_{AB} - ES \\ E_{AB} - ES & E_B - E \end{vmatrix} = 0$$

holds true. Assuming two identical nuclei, $Z_A = Z_B = Z$, we have $E_A = E_B$. The two solutions of the equation are

$$E_+ = \frac{E_A - E_{AB}}{1 - S}$$

$$E_- = \frac{E_A + E_{AB}}{1 + S}$$



These two solutions correspond to a bound state (E_-) and an antibonding state (E_+). $E_\pm$ play the role of the effective potential energy that drives the nuclear motion.

Is the Born Oppenheimer approximation valid when we describe the quantum mechanical behaviour of complex molecules? There is no general answer to this question. Referring to the example for H_2^+, we can only state that

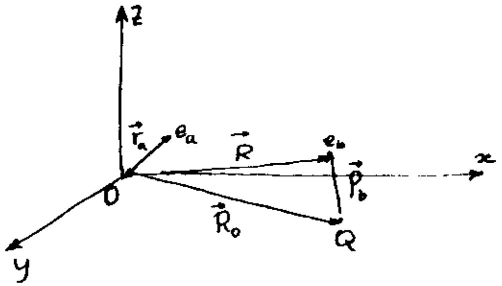
-) If the molecule is in the bound state, and the kinetic energy of the nuclei is small enough that molecular elongation does not exceed R_0, then the two energy levels E_+ and E_- are separated at all times, and transitions between them are unlikely to occur because of the nuclear motion. If this is the case, then the Born Oppenheimer approximation is valid.
-) When the interatomic separation exceeds R_1, the electron belongs either to the φ_A orbital or to the φ_B orbital, (unless we have been able to prepare the system in a superposition of the two orbitals!). In this case, transitions from φ_A to φ_B or viceversa are unlikely to occur (the probability for such transitions decays exponentially with R). Thus, in practice, we have a single state for the system (either φ_A or φ_B), and the Born-Oppenheimer approximation is still valid.
-) In the intermediate region, transitions between E_+ and E_- are likely to occur because of the nuclear motion. Here, the Born-Oppenheimer approximation is not valid, and one should use the general formulation instead.

The long range interatomic potentials.

When we deal with collisions, long range interatomic potentials play an important rôle. We will discuss briefly how these potentials arise and their effect on the nuclear motion.

The classical interatomic potential.

Choose a reference (cartesian) frame as in figure, with the origin at the nucleus of one atom, while the other atomic nucleus is in Q on the x-y plane



Charge e_a (electron or nucleus) belongs to atom in O. Displaced from O by $\vec r_a$

Charge e_b (electron or nucleus) belongs to atom in Q. Displaced from Q by $\vec\rho_b$.

The two nuclei are separated by $\vec R_0$, while $\vec R_b$ is the vector from O to e_b.

The electrostatic potential induced by the charges in atom O is

$$\varphi(\vec R) = \sum_a \frac{e_a}{|\vec R - \vec r_a|}$$

and the interatomic potential is

$$U = \sum_b e_b\, \varphi(\vec R_b).$$

Developing $|\vec R - \vec r_a|^{-1}$ in series of Legendre polynomials

$$\frac{1}{|\vec R - \vec r_a|} = \sum_0^\infty{}_\ell \frac{r_a^\ell}{R^{\ell+1}} P_\ell(\cos\chi_\ell) \qquad (R > r_a)$$

where χ_a = angle $\widehat{\vec R \vec r_a}$.

Then

$$\varphi(\vec R) = \sum_{\ell=0}^\infty \frac{1}{R^{\ell+1}} \left\{ \sum_a e_a r_a^\ell P_\ell(\cos\chi_a)\right\}.$$

The sum in braces is the multipole expansion of the potential generated by charges e_a at the point $\vec R$. For $\ell=0$, $P_0(\cos\chi_a) \equiv 1$, and the sum reduces to $\sum_a e_a$ i.e., the total charge of atom O, zero if the atom is neutral. For $\ell=1$, the sum reduces to $\sum_a e_a r_a \cos\chi_a$, i.e., the dipolar distribution of charges in atom O.

For simplicity, let us assume that the only term that survives in curly brackets is that with $\ell = 1$, all higher terms being zero.

We write this term as an effective dipole

$$\sum_a e_a r_a^\ell \cos\chi_a = \wp_0 \cos\chi\, \delta_{\ell 1}$$

Then $\varphi(\vec R) = \frac{\wp_0 \cos\chi}{R^2}$. We also write $\vec R$ as $\vec R_0 + \vec\rho$ (see figure); the

$$\varphi(\vec R_0, \vec\rho| = \frac{\wp_0}{|\vec R_0 + \vec\rho|^3}\left\{\alpha(x_0+\xi) + \beta(y_0+\eta) + \gamma(z_0+\zeta)\right\} =$$

$$= \wp_0 \left\{\alpha(x_0+\xi) + \beta(y_0+\eta) + \gamma(z_0+\zeta)\right\}\left\{\sum_0^\infty{}_k \frac{\rho^k}{R_0^{k+1}} P_k(\cos\psi)\right\}^3$$

where α, β, γ are direction cosine of the dipole moment in O and ψ is the angle between $-\vec R_0$ and $\vec\rho$. We have used the components $(x_0, y_0, z_0$ of $\vec R_0$ and (ξ, η, ζ) of $\vec\rho$.

<u>Note</u>. Although atom in O has a dipolar moment only, all spherical components appear in the expression for φ when developed around a different centre of symmetry.

Collecting terms with the same power dependence on R_0 in the expansion for φ, we get

$$\varphi(\vec R_0,\vec\rho) = \varphi_0(\vec R_0,\vec\rho) + \varphi_1(\vec R_0,\vec\rho) + \varphi_2(\vec R_0,\vec\rho) +$$

with

$$\varphi_0(\vec R_0,\vec\rho) = \frac{\vec{\mathcal P}_0\cdot\vec R_0}{R_0^3} \qquad \text{Dipole (in O) - Charge (in Q) interaction}$$

$$\varphi_1(\vec R_0,\vec\rho) = \frac{3\,\vec{\mathcal P}_0\cdot\vec R_0}{R_0^4}\,\rho\,P_1(\cos\psi) + \frac{\vec{\mathcal P}_0\cdot\vec\rho}{R_0^3} \qquad \text{Dipole-Dipole interaction}$$

$$\varphi_2(\vec R_0,\vec\rho) = \frac{3\vec{\mathcal P}_0\cdot\vec R_0}{R_0^5}\,\rho^2\left[P_0(\cos\psi) + P_1^2(\cos\psi)\right] + \frac{3\,\vec{\mathcal P}_0\cdot\vec\rho}{R_0^4}\,\rho\,P_1(\cos\psi) \qquad \text{Dipole-Quadrupole interaction.}$$

and so on.

Summation over e_b will cancel some of these terms, depending on the symmetry of charge distribution around Q. We assume that the only surviving term is again the dipolar term. Thus

$$U_1 = \sum_b e_b\,\varphi(\vec R_0,\vec\rho_b) = \sum_b e_b\,\varphi_1(\vec R_0,\vec\rho_b)$$

yielding

$$U_1 = \frac{\vec{\mathcal P}_0\cdot\vec{\mathcal P}_Q - 3(\vec{\mathcal P}_0\cdot\vec R_0)(\vec{\mathcal P}_Q\cdot\vec R_0)}{R_0^3}$$

with

$$\vec{\mathcal P}_Q = \sum_b e_b\,\vec\rho_b .$$

According to classical mechanics, dipole-dipole interaction may arise only if charges have a dipole moment in each atom, namely the sums $\sum_b e_b\vec\rho_b$, $\sum_a e_a\vec r_a$ do not vanish. So that, if the charge distribution were spherically symmetric for both atoms, with $\sum e_a = \sum e_b = 0$ (neutral atoms), there would have been <u>no interaction at all</u>.

In quantum mechanics, this is no longer true. Two atoms, both in the ground, spherically symmetric state, may have a dipole-dipole (or higher) interaction. This is due to quantum fluctuations as we will see immediately.

<u>The quantum mechanical interatomic potential.</u>

In quantum mechanics, the determination of the interatomic potentials are only half of the problem. We must also determine the quantum mechanical state in which the atomic system is. We will do that using the Born-Oppenheimer approximation.

Define:

$\vec q_A$, $\vec Q_A$ electronic and nuclear coordinates of atom A

$\vec q_B$, $\vec Q_B$ " " " " of atom B.

Total hamiltonian

$$H = H_A(\vec q_A,\vec Q_A) + H_B(\vec q_B,\vec Q_B) + V_{AB}(\vec q_A,\vec Q_A,\vec q_B,\vec Q_B).$$

with

$$H_A(\vec q_A,\vec Q_A) = \hat T_n^{(A)} + \hat T_e^{(A)} + V_{ne}^{(A)} + V_{ee}^{(A)}$$

and a similar expression for H_B. The interaction term V_{AB} is the quantum analog of the classical term U discussed above.

The Born Oppenheimer approximation is now applied. We write for the molecular system formed by the two atoms

$$\Psi(\vec{q}_A, \vec{Q}_A, \vec{q}_B, \vec{Q}_B) = \Phi_{AB}(\vec{q}_A, \vec{Q}_A, \vec{q}_B, \vec{Q}_B)\, \chi_{AB}(\vec{Q}_A, \vec{Q}_B)$$

and find the eigenvalue W for the electronic configuration by solving

$$\left[\hat{T}_e^{(A)} + \hat{T}_e^{(B)} + V_{ne}^{(A)} + V_{ne}^{(B)} + V_{ee}^{(A)} + V_{ee}^{(B)} + V_{AB} \right] \phi_{AB} = W\, \phi_{AB} .$$

<u>Note</u> The term V_{nn} has been included in the electronic equation, in contrast with what has been done above.

Then we have, for the nuclear wavefunction

$$\left\{ \hat{T}_n^{(A)} + \hat{T}_n^{(B)} + W(\vec{Q}_A, \vec{Q}_B) \right\} \chi_{AB} = E\, \chi_{AB} .$$

The molecular wavefunctions for this case of well separated atoms are normally built starting from the free atom wavefunctions ϕ_A, ϕ_B, χ_A and χ_B.

$$\Phi_{AB}(\vec{q}_A, \vec{Q}_A, \vec{q}_B, \vec{Q}_B) = \sum_{l,n} c_{AB}^{(ln)}(\vec{Q}_A, \vec{Q}_B)\, \Phi_A^{(l)}(\vec{q}_A)\, \Phi_B^{(n)}(\vec{q}_B)$$

where $\Phi_A(\vec{q}_A)$, $\Phi_B(\vec{q}_B)$ are eigenfunctions of H_A, H_B respectively

[<u>Note</u> Φ_A does not depend on $\vec{Q}_A$].

$$\chi_{AB}(\vec{Q}_A, \vec{Q}_B) = \sum_{ij} d_{AB}^{(jk)}(\vec{Q}_A, \vec{Q}_B)\, \chi_A^{(j)}(\vec{Q}_A)\, \chi_B^{(k)}(\vec{Q}_B)$$

where $\chi_A^{(j)}(\vec{Q}_A)$ $[\chi_B^{(k)}(\vec{Q}_B)]$ are eigenfunctions of $\hat{T}_n^{(A)}$ $[\hat{T}_n^{(B)}]$. This forms the basis for the 'partial waves expansion' used in scattering theory.

Let us examine in detail the case that V_{AB} is a dipole-dipole interacti

$$V_{AB} = \frac{\vec{p}_A \cdot \vec{p}_B - 3(\vec{p}_A \cdot \vec{R}_0)(\vec{p}_B \cdot \vec{R}_0)\, R_0^{-2}}{R_0^3} .$$

It is convenient to pass to the tensorial form of scalar products. The scalar product of two vectors in tensorial form is

$$\vec{u} \cdot \vec{v} = \frac{4\pi}{3} |\vec{u}|\, |\vec{v}| \sum_{-1}^{1} {}_m\, Y_{1m}^*(\theta_u, \varphi_u)\, Y_{1m}(\theta_v, \varphi_v)$$

where $Y_{lm}(\theta, \varphi)$ are the spherical harmonic functions of rank l, and the relationships

$$u_x = |\vec{u}| \sin\theta_u \cos\varphi_u$$
$$u_y = |\vec{u}| \sin\theta_u \cos\varphi_u$$
$$u_z = |\vec{u}| \cos\theta_u$$

exist between the cartesian (u_x, u_y, u_z) and spherical $(|\vec{u}|, \theta_u, \varphi_u)$ components.

Then

$$V_{AB} = \frac{4\pi\, p_A\, p_B}{3 R_0^3} \left\{ \sum_{-1}^{1} {}_m\, Y_{1m}^*(\theta_A, \varphi_A)\, Y_{1m}(\theta_B, \varphi_B) + \right.$$
$$\left. - 3\, Y_{1,0}^*(\theta_A, \varphi_A)\, Y_{1,0}(\theta_B, \varphi_B) \right\}$$

in which we have chosen $\vec{R}_0$ as the quantisation (polar) axis, and we have used

$$Y_{1,0}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta = \frac{R_z}{R}\sqrt{\frac{3}{4\pi}}.$$

Single-electron, free atom wavefunctions $\phi_A(\vec{q}_A)$ and $\phi_B(\vec{q}_B)$ can also be expressed in terms of spherical harmonic functions:

For an S- atomic state, with zero orbital angular momentum L,

$$\Phi^{(0)}(\vec{q}) = g_0(q)\,Y_{0,0}(\theta,\varphi) \equiv g_0(q)$$

For a P- atomic state, with $L = 1$, we have three orthogonal (i.e., linearly independent) wavefunctions

$$\Phi^{(1,1)}(\vec{q}) = g_1(q)\,Y_{1,1}(\theta,\varphi)$$

$$\Phi^{(1,0)}(\vec{q}) = g_1(q)\,Y_{1,0}(\theta,\varphi)$$

$$\Phi^{(1,-1)}(\vec{q}) = g_1(q)\,Y_{1,-1}(\theta,\varphi)$$

and so on.

Using this representation, the matrix elements of V_{AD} can be easily evaluated by means of the formula (the Gaunt formula)

$$\int Y^*_{l'm'}(\theta,\varphi)\,Y_{LM}(\theta,\varphi)\,Y_{lm}(\theta,\varphi)\,d\Omega =$$
$$= (-1)^{m'}\sqrt{\frac{(2l'+1)(2L+1)(2l+1)}{4\pi}}\begin{pmatrix} l' & L & l \\ -m' & M & m \end{pmatrix}\begin{pmatrix} l' & L & l \\ 0 & 0 & 0 \end{pmatrix}$$

$[d\Omega = \sin\theta\, d\theta\, d\varphi]$,

where $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ are the so-called 3-j symbols, that are closely related to the Clebsch Gordan (CG) coefficients met in the theory of coupling of angular momenta.

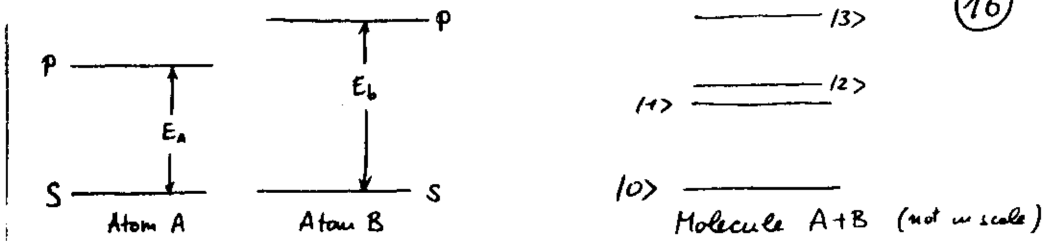
The 3-j symbol $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ is zero if $d+e+f \neq 0$, or if a, b, c do not obey the triangular condition. These properties set selection rules in the determination of non vanishing matrix elements.

We pass now to the construction of molecular electronic wavefunctions. For simplicity, we assume that

Atom A has two states only, $|\phi_A^s\rangle$; $l=0,\ m=0$
$|\phi_A^p\rangle$ $l=1,\ m=0$
Atom B has two states only, $|\phi_B^s\rangle$ $l=0,\ m=0$
$|\phi_B^p\rangle$ $l=1,\ m=0$

Four molecular states can be built from these atomic states.

$|0\rangle = |\phi_A^s\rangle|\phi_B^s\rangle$ Energy E_0
$|1\rangle = |\phi_A^p\rangle|\phi_B^s\rangle$ Energy E_1
$|2\rangle = |\phi_A^s\rangle|\phi_B^p\rangle$ Energy E_2
$|3\rangle = |\phi_A^p\rangle|\phi_B^p\rangle$. Energy E_3.



The selection rules allow us to find the nonvanishing matrix elements of V_{AB}; these are $\langle 0|V_{AB}|3\rangle$ and $\langle 1|V_{AB}|2\rangle$.
In the compound atomic states basis the Hamiltonian H has the representation

$$H = \begin{pmatrix} E_0 & V_{03} & 0 & 0 \\ V_{30} & E_3 & 0 & 0 \\ 0 & 0 & E_1 & V_{12} \\ 0 & 0 & V_{21} & E_2 \end{pmatrix}.$$

This Hamiltonian can be easily diagonalized because of its block structure. If the two atoms were initially (at $R=\infty$) in their ground states, when they come to a finite mutual distance, the electronic configuration follows adiabatically the change of R and the ground energy level - i.e. the eigenvalue of H that develops out of E_0 - is

$$E_0' = \frac{E_3 + E_0 - \sqrt{(E_3-E_0)^2 + 4|V_{03}|^2}}{2}.$$

Since $|V_{03}|$ is usually much smaller than the energy separation $E_3 - E_0$, we find

$$E_0' \sim E_0 - \frac{|V_{03}|^2}{E_3 - E_0} \qquad (E_0' < E_0)$$

To a decrease in energy corresponds an 'attracting' force:

$$F = \frac{\partial}{\partial R}\frac{|V_{03}|^2}{E_3 - E_0}.$$

Since V_{03} depends on R with the power law R^{-3}, the interaction potential energy depends on R^{-6} and the force on R^{-7}.
A perturbative calculation that included all higher states would have yielded

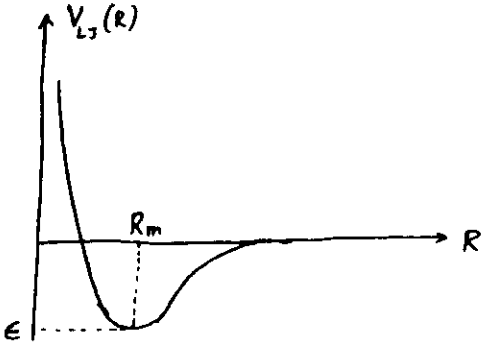
$$E_0' \approx E_0 - \sum_k \frac{|\langle 0|V_{AB}|k\rangle|^2}{E_k - E_0}$$

This attracting force, which acts even between two spherically symmetric ~~states~~ charge distributions, such as the atoms in S-states is called the London dispersion force, or van der Waals force.

At shorter interatomic distances, the London dispersion force is superseded by repulsive forces. The transition from the attractive domain to the repulsive one is usually described by model potential functions. In some cases, the potential energy function has been evaluated numerically, starting from first principles.
A typical model potential that asymptotically tends to the R^{-6} behaviour for large R is the so called Lennard-Jones n-6 potential

$$V_{LJ}(R) = \epsilon\left[\frac{6}{n-6}\left(\frac{R_m}{R}\right)^n - \frac{n}{n-6}\left(\frac{R_m}{R}\right)^6\right]$$

where n (not necessarily integer, but greater than 6), ϵ and R_m are fitting parameters. The exponent n is often given the value 12.



The Lennard-Jones model potential.

Note The potential functions described so far depend only on the interatomic separation R, not on the direction in space of $\vec{R}$ relative to the two atoms. This is a consequence of the assumption we made about the ground state of the atoms in which they are initially prepared – an S, spherically symmetric state.

Vhen the interatomic potential energy is a simple function of $|\vec{R}|$, as in our case, we can even attempt at solving the Schrödinger equation for the nuclear motion,

$$\left\{\hat{T}_n^{(A)} + \hat{T}_n^{(B)} + W(R)\right\}\chi_{AB} = E\chi_{AB}.$$

Ve write this equation in relative spherical polar coordinates, $R = |\vec{Q}_A - \vec{Q}_B|$, θ = angle between $\vec{R}$ and the z-axis, φ = angle between the projection of $\vec{R}$ onto the plane x-y, and the x-axis:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial \chi}{\partial R}\right) + \frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\chi}{\partial\theta}\right) + \frac{1}{R^2\sin^2\theta}\frac{\partial^2\chi}{\partial\varphi^2}\right] + W(R)\chi_{AB} =$$
$$= E\chi_{AB}$$

where μ is the reduced mass of the two nuclei, $\mu = M_A M_B/(M_A+M_B)$.

By separation of variables in χ_{AB}

$$\chi_{AB}(R,\theta,\varphi) = \psi(R)\,Y(\theta,\varphi)$$

we find

$$-\frac{\hbar^2}{2\mu R^2\psi}\frac{\partial}{\partial R}\left(R^2\frac{\partial\psi}{\partial R}\right) + W(R) - E = -\frac{\hbar^2}{2\mu R^2 Y}\hat{L}^2 Y \equiv \lambda$$

where $\hat{L}^2$ is the square angular momentum operator divided by $\hbar^2$:

$$\hat{L}^2 = -\frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right].$$

We know that $\hat{L}^2$ has the eigenvalues $L(L+1)$, with L integer ≥ 0. Hence the radial equation for ψ is

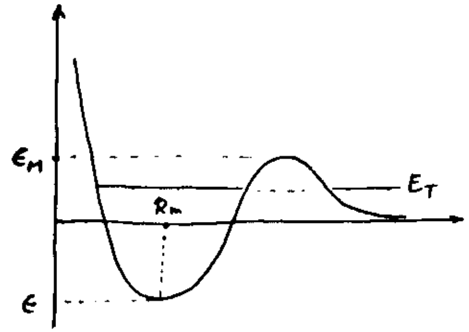
$$-\frac{\hbar^2}{2\mu}\frac{1}{R^2}\frac{d}{dR}\left(R^2\frac{d\psi}{dR}\right) + \left[W(R) + \frac{\hbar^2 L(L+1)}{2\mu R^2}\right]\psi = E\psi,$$

i.e., it describes the motion of a particle with mass μ in an effective potential

$$U(R) = W(R) + \frac{\hbar^2}{2\mu}\frac{L(L+1)}{R^2}.$$

The term $\frac{\hbar^2}{2\mu}\frac{L(L+1)}{R^2}$, known as the 'centrifugal potential', is a repulsive potential that arises because of the relative angular momentum of the two atoms.

The resulting graph is shown in the figure. When $L \neq 0$, a bound state (a van der Waals molecule) can be formed starting from atoms with a kinetic energy at $R = \infty$ less than ϵ_M.



The effective interatomic potential including the centrifugal potential. Atoms with kinetic energy E_T at $R=\infty$ can be trapped.

Tunneling or collision with a third atom is required either to form or dissociate the van der Waals molecule.

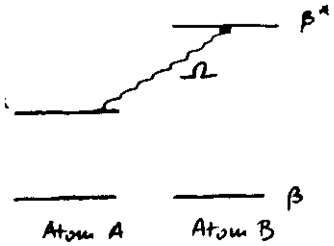
Atomic collisions in the presence of a laser field.

Coupling with the field is now introduced into our Hamiltonian. We consider here only electric dipole coupling.

$$H = H_A + H_B + V_{AB} - \vec{E}(\vec{Q}_A)\cdot\hat{\vec{P}}_A - \vec{E}(\vec{Q}_B)\cdot\hat{\vec{P}}_B .$$

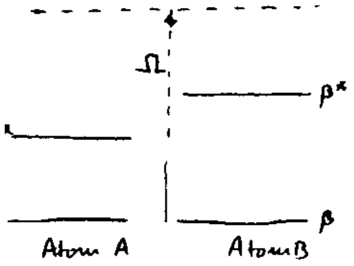
The semiclassical description of the field is used, in which the field is considered as a classical field. $\hat{\vec{P}}_A$ and $\hat{\vec{P}}_B$ are the atomic dipole moment operators of atoms A and B, that we already met in the discussion of the quantum mechanical description of interatomic potentials.
In principle, one should evaluate the field at the points where the electric dipoles are, namely at $\vec{Q}_A$ and $\vec{Q}_B$. However we are interested here only in the effects of the field on the atomic collision, i.e. over a range of interatomic distances in which V_{AB} is appreciably different from zero. These distances are actually only a fraction of the optical wavelength of the field. Hence we can assume $\vec{E}(\vec{Q}_A) \simeq \vec{E}(\vec{Q}_B)$ when $\vec{Q}_A$ and $\vec{Q}_B$ are the coordinates of two colliding atoms.

The field is assumed to be weak - we have some control over its intensity, indeed. Not so for the collisions, that may occur at any impact parameter and involve also strong atomic interactions. Thus, we must first diagonalize the collisional hamiltonian, and find the molecular (adiabatic) states, and then evaluate the transition probabilities among those molecular states, induced by the field. We refer to these effects as collisionally aided radiative processes. In the next page are represented several processes of this kind.



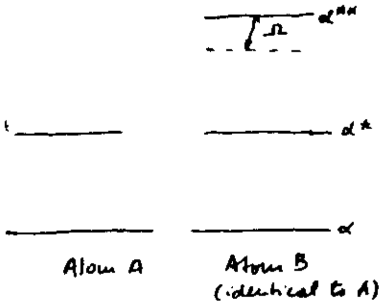
Reaction 1

$$A(\alpha^*) + B(\beta) + \hbar\Omega \rightarrow A(\alpha) + B(\beta^*)$$



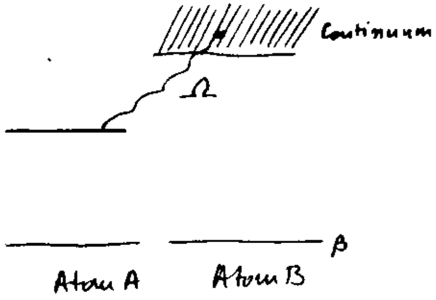
Reaction 2

$$A(\alpha) + B(\beta) + \hbar\Omega \rightarrow A(\alpha^*) + B(\beta^*)$$



Reaction 3

$$\hbar\Omega + A(\alpha^*) + A(\alpha^*) \rightarrow A(\alpha) + A(\alpha^{**})$$



Reaction 4

$$A(\alpha^*) + B(\beta) + \hbar\Omega \rightarrow A(\alpha) + B^+ + e^-$$

All these reactions occur during a collision between the two atoms and in the presence of a laser field. An incorrect interpretation of reaction 2, as a reaction involving separated, non interacting atoms, would lead to the conclusion that a fraction of a photon has been absorbed by atom A and the other fraction by atom B.

Other processes may lead to molecular dissociation or to the creation of a chemical bond with the formation of a molecule.

In order to evaluate the transition probability for these reactions, we can exploit these facts:

- Electrons move much faster than atomic nuclei, and the electronic configuration adiabatically follows changes of the interatomic distances. This is the Born-Oppenheimer approximation.
- The nuclei are bulky objects, and their motion is classically described.
- The atoms move on the potential energy surface pertaining to the initial state in which atoms are prepared.

The final assumption concerns the electromagnetic (laser) field:

The field is weak enough so that it does not induce appreciable modifications to the collisional model based on the preceding assumptions. In particular, transitions induced by the field can be treated as a 'small leakage' of population out of the molecular state, and calculated by first order perturbation theory.

Motion of the nuclei.

The classical equations of motion for the nuclei are

$$M_X \ddot{\vec{Q}}_X = - \text{grad}_X W(\vec{Q}_A, \vec{Q}_B) \qquad (X = A, B).$$

The force $-\text{grad} W$ can be calculated from the knowledge of the interparticle potentials and the electronic wavefunction $\Phi_{AB}(\vec{q}_A, \vec{Q}_A, \vec{q}_B, \vec{Q}_B)$ of the Born-Oppenheimer approximation. This is the Hellmann-Feynman theorem. We have, for $\vec{F}_A$:

$$\vec{F}_A = -\frac{\partial W}{\partial \vec{Q}_A} = -\frac{\partial}{\partial \vec{Q}_A} \int d\vec{q}_A d\vec{q}_B\, \Phi^*_{AB} (H_A + H_B + V_{AB}) \Phi_{AB} =$$

$$= -\int d\vec{q}_A d\vec{q}_B\, \frac{\partial \Phi^*_{AB}}{\partial \vec{Q}_A} (H_A + H_B + V_{AB}) \Phi_{AB} - \int d\vec{q}_A d\vec{q}_B\, \Phi^*_{AB} (H_A + H_B + V_{AB}) \frac{\partial \Phi_{AB}}{\partial \vec{Q}_A}$$

$$- \int d\vec{q}_A d\vec{q}_B\, \Phi^*_{AB} \left[\frac{\partial}{\partial \vec{Q}_A} (H_A + H_B + V_{AB}) \right] \Phi_{AB} .$$

The first two terms cancel because $H_A + H_B + V_{AB}$ is hermitean, and Φ_{AB} is normalized to unit for any value of $\vec{Q}_A$ and $\vec{Q}_B$:

$$\int d\vec{q}_A d\vec{q}_B \left\{ \left[\frac{\partial \Phi^*_{AB}}{\partial \vec{Q}_A} (H_A + H_B + V_{AB}) \Phi_{AB} + \left[(H_A + H_B + V_{AB}) \Phi^*_{AB} \right] \Phi_{AB} \right\} =$$

$$= W(\vec{Q}_A, \vec{Q}_B) \frac{\partial}{\partial \vec{Q}_A} \int d\vec{q}_A d\vec{q}_B\, \Phi^*_{AB} \Phi_{AB} = 0.$$

Then

$$\vec{F}_A = - \int d\vec{q}_A d\vec{q}_B\, \Phi^*_{AB} \left(\frac{\partial V_{ne}^{(A)}}{\partial \vec{Q}_A} + \frac{\partial V_{ne}^{(B)}}{\partial \vec{Q}_A} + \frac{\partial V_{AB}}{\partial \vec{Q}_A} \right) \Phi_{AB} ,$$

and a similar expression for $\vec{F}_B$.

Note. We have not included the atom-field interaction in the Hamiltonian since we <u>have assumed</u> that the field is <u>weak</u>. On the other hand, for a <u>strong</u> field, the same assumption of validity for the Born-Oppenheimer approximation would be questionable.

Physical interpretation of the force $\vec{F}_A$: there is the expectation value of the interparticle force, $-\left\langle \frac{\partial V_{AB}}{\partial \vec{Q}_A} \right\rangle$, and this is obvious. Next, there is the term $-\left\langle \frac{\partial V_{ne}^{(A)}}{\partial \vec{Q}_A} \right\rangle$, (the other term $-\left\langle \frac{\partial V_{ne}^{(B)}}{\partial \vec{Q}_A} \right\rangle$ vanishes identically). This term would vanish(†) if $\Phi_{AB} = \phi_A(\vec{q}_A)\, \phi_B(\vec{q}_B)$, i.e. if the two atoms were non interacting.

When the collisional interaction arises, the atoms are stretched and a net force on the atomic nucleus results.

Since the interatomic potential V_{AB} depends on $\vec{Q}_A - \vec{Q}_B$,

$$\vec{F}_A + \vec{F}_B = 0$$

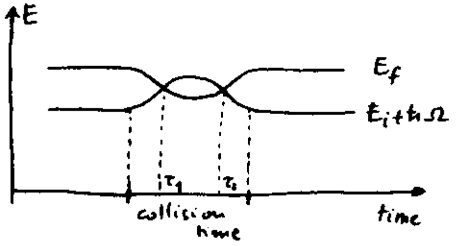
as expected for an isolated system.

We have already seen how to construct the molecular wavefunctions for the electronic configuration when the atoms are separated by a distance R. This in turn enables us to evaluate the forces applied onto the atoms, which drive the atomic motion.

(†) Actually, in an isolated atom, there is no force acting on its centre of mass. For practical purpose, however, the centre of mass of the atom can be considered at the atomic nucleus.

The function $R(t)$ can then be found by integrating the equations of motion.

Once the collisional problem has been solved, we can look at the transitions induced by the field. In the figure are reported the energies $E_i + \hbar\Omega$ (initial state energy + photon energy) an E_f (energy of the state to which transition is aimed), as a function of time. It must be stressed that both of them are evaluated along the atomic trajectory determined by the potential of the initial state.



In the figure we have shown a typical situation of an off resonance laser frequency. When the atoms are very far apart, the laser frequency does not match the frequency difference between the initial and final states. During the collision, the energy levels are displaced and instantaneous frequency matching occurs at τ_1 and τ_2. The transition probability can be evaluated by applying first order perturbation theory at the points of level crossing.

An example of calculation of transition probabilities.

Consider the process of reaction 1 at page 22. The initial state in which the system is prepared is $|\alpha^*\rangle|\beta\rangle$, and the final state of the reaction is $|\alpha\rangle|\beta^*\rangle$. The molecular state that develops out of the initial state during the collision will be a superposition of states connected to $|\alpha^*\rangle|\beta\rangle$ by V_{AB}, at any order. The final state need not be among them.
If we consider only first order contributions, we have, for the molecular state

$$|\psi\rangle = |a_i\rangle + \sum_j d_{ij}\,|a_j\rangle .$$

where $|a_i\rangle = |\alpha^*\rangle|\beta\rangle$ and $|a_j\rangle$ is a generic state for which

$$\langle a_i|\, V_{AB}\,|a_j\rangle \neq 0.$$

Let us pick up a particular state $|a_j\rangle$ among this set of states, with the requirement that $|a_j\rangle$ must be connected also to the final state $|a_f\rangle = |\alpha\rangle|\beta^*\rangle$ either by the operator $-\vec{p}_A \cdot \vec{E}$ or by the operator $-\vec{p}_B \cdot \vec{E}$.
We write the Schrödinger time dependent equation for the amplitudes of these three states, $|a_i\rangle$, $|a_j\rangle$ and $|a_f\rangle$.

$$i\dot{a}_j = \omega_j a_j + V_{ji}\,a_i + \chi e^{i\Omega t} a_f$$

$$i\dot{a}_i = \omega_i a_i + V_{ij}\,a_j$$

$$i\dot{a}_f = \omega_f\, a_f + \chi e^{-i\Omega t} a_j .$$

These equations have been written in the Rotating Wave Approximation; the atom-field coupling χ may be considered constant throughout the short duration of the collisional interaction.

In this very simple scheme, the molecular states can be found by diagonalizing the matrix

$$\underset{\sim}{A} = \begin{pmatrix} \omega_j & V_{ji} \\ V_{ij} & \omega_i \end{pmatrix},$$

assuming V_{ij} constant. The eigenvectors of $\underset{\sim}{A}$ represent the instantaneous (adiabatic) states of the molecule formed during the collision. This is, of course, in the spirit of the Born-Oppenheimer approximation.
The eigenvalue of $\underset{\sim}{A}$ that goes to ω_i when $V_{ji} \to 0$, is the displaced energy level E_i that we need consider. If the final energy level E_f undergoes significant displacement during the collision, that one should include other levels into the treatment.

When the instantaneous energy difference $E_f(t) - E_i(t)$ matches the photon energy $\hbar\Omega$ we have level crossing and the transition occurs.
We show now how to calculate transition probabilities, in the case in which perturbation theory can be applied to both collisional and atom-field interactions.
Since at first order the population of the initial level is not affected by both interactions, we can take

$$a_i \sim e^{-i\phi_i - i\omega_i t}$$

at all times during the collision. $\dot{\phi}_i$ represents the frequency

displacement of the initial level during the collision.
Replacing this expression for a_i in the equation for $\dot{a}_j$, and neglecting there the term $\chi e^{i\Omega t} a_f$, which is of higher order, we find

$$a_j \sim -i\, e^{-i\omega_j t} \int V_{ji}(t') \exp\{i[\omega_j t' - \omega_i t' - \phi_i]\}\, dt'.$$

Perturbation theory can be applied to the collisional problem only if $|\omega_j - \omega_i - \dot{\phi}_i| \gg |V_{ji}|$, see the discussion of the London dispersion force. Moreover, V_{ji} is assumed, as usual, to be slowly varying with time. Then we find, by integration

$$a_j \sim -\frac{V_{ji}\, e^{-i\omega_i t - i\phi_i}}{\omega_j - \omega_i - \dot{\phi}_i} \approx \frac{-V_{ji}\, a_i}{\omega_j - \omega_i}.$$

This expression, substituted in the equation for $\dot{a}_i$ in place of a_j, gives the functions $\dot{\phi}_i$

$$\dot{\phi}_i = \frac{-|V_{ij}|^2}{\omega_j - \omega_i}.$$

Then, from the equation for $\dot{a}_f$, we get the transition probability

$$|a_f(+\infty)|^2 = \chi^2 \left| \int_{-\infty}^{+\infty} dt' \, \frac{V_{ji}(t)}{\omega_j - \omega_i} \, e^{i\left[(\omega_f - \omega_i - \Omega)t' + \int_{-\infty}^{t'} \frac{|V_{ij}|^2}{\omega_j - \omega_i} dt''\right]} \right|^2$$

This formula shows that transitions are possible only when χ and V are $\neq 0$ simultan
Level crossing occurs when the phase of the integrand function in the expression for $|a_f(+\infty)|^2$ is stationary, i.e. when

$$\omega_f = \omega_i + \frac{|V_{ij}|}{\omega_i - \omega_j} + \Omega$$

If $\omega_i > \omega_j$, transitions occurs only for $\Omega < \omega_f - \omega_i$, i.e., in he 'red' side of the resonance $\omega_f - \omega_i$. This asymmetry in the spectral lineshape is characteristic of these processes.

The total cross section can be obtained by averaging $|a_f(+\infty)|^2$ over the collisional parameters, namely over the impact parameter and the relative velocity.

Concluding remarks.

In the reactions described in these lectures, off resonance transitions are made possible by the displacements of molecular energy levels induced by collisional interactions. It is evident that the energy defect (excess) must be supplied by (transferred to) the motional degrees of freedom, by means of the coupling mechanism that we have outlined in our lectures. Thus, these processes are accompanied by *cooling* or *heating* of the translational-vibrational degrees of freedom. However, to improve efficiency, one should use strong laser fields - and this poses difficulties for a correct theoretical description.

In fact, at strong laser intensities, the simple models discussed so far are not valid anymore:

•) the Born-Oppenheimer approximation becomes questionable, since at least two adiabatic states are involved - see the discussion of the LCAO method

•) the molecule is, under the effects of a strong laser field, in a superposition of states, and to each state corresponds a different potential energy surface. How is the nuclear motion affected by this fact?

In other words, the process becomes much more complicated because we cannot separate the collisional interaction from the atom-field interaction.

Nonetheless, this field of research is under active investigations, and its potentialities are still to be fully explored.

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