

MOLECULES

Molecules differ from atoms in the main because of the fact that the potential seen by the electrons lacks a central character. Even for the simplest of molecules, the homonuclear diatomic molecule, the potential is two-centred.

Although the general principles from atomic structure calculations still apply, the problem is considerably harder due to the multi-centre nature of the attractive potential. In atoms each electron contributes a simple $-Z/r$ term to the Hamiltonian, but in molecules there are as many terms as the number of nuclei.

The problem can be considerably simplified, however, if we take into account the large difference in the masses of the nuclei and the electrons. A key role is played by this fact in the analysis of molecular structure and spectra.

To begin let us compare the energies and masses of the electrons and the nuclei in a molecule.

for $m_e = 1$, $m_N \sim 2000$.

To estimate the momenta of the electrons let us consider them to be in a potential well of size R , the so-called bond-length, or size of the molecule. Then $p \sim \hbar/R$, so that

$E_e \approx \frac{\hbar^2}{2mR^2}$ is an order of magnitude estimate of electron energy.

In the following we consider only a diatomic molecule, for simplicity.

The energy of the nucleus, on the other hand, can be estimated by treating the molecule [specifically a diatomic molecule] as a linear harmonic oscillator, (which is bound due to the electronic attraction, but would fly apart due to nuclear repulsion in the absence of electrons)

The energy of this oscillator would be $\frac{1}{2} M \omega_{\text{vib}}^2 \delta^2$ where ω and δ are the frequency of oscillation and the displacement, respectively.

In the extreme case when the oscillation of the nuclear pair

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results in dissociation, the energy of the oscillator must be of the order of the electronic energy, since the balance of the two is what keeps the molecule together. (energies)

In this limit, $M\omega_{\text{vib}}^2 R^2/2 \sim E_e$, (dissociating limit) ||
 ~~E_{vib}~~ = hence $\hbar\omega_{\text{vib}} \sim \left(\frac{m}{M}\right)^{1/2} E_e$ (bound state estimate) ||

Thus, the energy of nuclear oscillations (called vibrational energy) is considerably smaller ($\sim 1\%$) of the electronic energy.

The nuclei have another degree of freedom, namely rotation.

If we treat, approximately, the nucleus pair as a rigid rotator, the quantised energy levels would be given by ~~the~~ $l(l+1)\hbar^2/2I$ where I is the moment of inertia, $MR^2/2$.

Thus $E_{\text{rot}} \approx \frac{\hbar^2}{I} \approx \frac{m}{M} E_e$ |

Thus, $E_{\text{rot}} < E_{\text{vib}} < E_{\text{elec}}$
 and the scaling of the order of magnitude is $\sim (m/M)^{1/2} \approx 10^{-2}$

This stark difference in the energies allows us to separate the three kinds of motion, and considerably simplify the problem of solving the Schrödinger equation for a molecule. The difference in energies corresponds to a difference in the characteristic time of the motions.

Although we have considered the case of a diatomic molecule, the same considerations apply to polyatomic molecules.

The solution to the Schrödinger equation of a molecule based by the separation of electronic, vibrational and rotational degrees of motion (based on the energy / time scale differences considered above) is called the Born-Oppenheimer approximation.

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We write the Hamiltonian as a sum of 2 parts

$$\boxed{\hat{H} = \hat{H}_{el} + \hat{T}_N \quad \text{where} \quad \hat{H}_{el} = \hat{T}_e + \hat{V}}$$

and first obtain the electronic basis set $\{\Phi\}$, whose elements are eigenfunctions of the electronic Hamiltonian

$$\boxed{(\hat{T}_e + \hat{V}) \Phi_a = E_a \Phi_a \quad ; \quad (\Phi \equiv \Phi_a(\vec{R}; \vec{r}_1, \vec{r}_2, \dots, \vec{r}_n))}$$

Thus the electronic wavefunctions have a parametric dependence on the internuclear separation \vec{R} (only scalar value, not vectorial)

For each fixed R , the set Φ is a complete ^{orthonormal} basis set

$$\langle \Phi_a | \Phi_b \rangle = \delta_{ab}$$

The energy eigen values E_a depend on $|R|$ parametrically; They do not depend on the vectorial nature of R

We can now obtain the complete molecular wavefunction Ψ by expansion in terms of the set Φ :

$$\boxed{\Psi(\vec{R}, \{\vec{r}_i\}) = \sum_a F_a(\vec{R}) \Phi_a(\vec{R}; \{\vec{r}_i\})}$$

↑
These functions describe pure nuclear motion
i.e. they describe vibration and rotation for
a given electronic state

SOLUTION FOR NUCLEAR MOTION

We now solve the complete Schrödinger eqn to obtain a solution for F_a ; this solution will then yield Ψ .

The complete Schrödinger eqn is

$$(\hat{H}_e + \hat{T}_n) \Psi = E \Psi \quad ; \quad (\Psi \equiv \Psi(\vec{R}, \{\vec{r}_i\}))$$

$$\therefore (\hat{H}_e + \hat{T}_n) \sum_a F_a(\vec{R}) \Phi_a(\vec{R}; \{\vec{r}_i\}) = E \sum_a F_a(\vec{R}) \Phi_a(\vec{R}; \{\vec{r}_i\})$$

We can now project this equation on successive vectors of the basis set $\{\Phi\}$ and obtain the set of equations

$$\sum_b \langle \Phi_a | \hat{T}_n + \hat{H}_e - E | \Phi_b \rangle F_b(\vec{R}) = 0$$

$$\sum_a \langle \Phi_b | \hat{T}_n + \hat{H}_e - E | \Phi_a \rangle F_a(\vec{R}) = 0 \quad \left\{ \begin{array}{l} \text{By projecting on } \Phi_b; \\ b = 1, 2, 3, \dots \end{array} \right.$$

Recalling that $\hat{H}_e \Phi_a = E_a \Phi_a$, $\langle \Phi_b | \Phi \rangle = \delta_{ab}$ and replacing \hat{T}_n by the full operator for the nuclear K.E. we get

$$\sum_a \langle \Phi_b | \left[-\frac{\hbar^2}{2m} \left[\frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \right] + \frac{-\hbar^2}{2\mu R^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] | \Phi_a \rangle F_a(\vec{R}) + (E_b(R) - E) F_b(\vec{R}) = 0$$

$$\text{i.e. } \sum_a \langle \Phi_b | \hat{T}_n | \Phi_a \rangle F_a(R) + [E_b(R) - E] F_b(\vec{R}) = 0 \quad \{ b = 1, 2, 3, \dots \}$$

complete electronic basis set with parametric R dependence
 nuclear KE operator
 nuclear motion wave function
 electronic energy eigenvalue
 total energy of the molecule.

(NOTE Φ_a & F_a are both functions of \vec{R})
 $\vec{K} \rightarrow$ nuclear ang. mom
 $\vec{L} \rightarrow$ electronic ang. mom

NOTE:
 $\hat{T}_n = -\frac{\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\hat{K}^2}{2\mu R^2} \right]$
 where $\hat{K}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$

▶ This is an infinite set of coupled equations, and this set of equations is exactly identical to the full Schrödinger equation.

▶ We now introduce the Born-Oppenheimer or the adiabatic approximation which acknowledges the fact that nuclear motion is slow compared to the electronic motion.

▶ As a consequence, the electronic wavefunctions Φ_a vary very slowly w.r.t. \vec{R} as \vec{R} changes (\vec{r}_i change rapidly in comparison)

Thus, we can treat $|\partial\Phi_a/\partial R| \rightarrow 0$ in comparison to $|\partial F_a/\partial R|$

Hence we neglect the $\partial\Phi_a/\partial R$ term

We also neglect the off-diagonal terms of $K\hat{L}^2$, since the Φ_a do not change much with the ^{angular} nuclear motion and $\langle\Phi_a|\Phi_b\rangle = 0$

When we neglect these terms the equations get decoupled to yield

$$\left[\frac{-\hbar^2}{2\mu} \left(\frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \langle\Phi_b|K\hat{L}^2|\Phi_b\rangle + E_b(R) - E \right] F_b(\vec{R}) = 0$$

$F_b(R)$ is thus the nuclear motion wavefunction for a given electronic state Φ_b

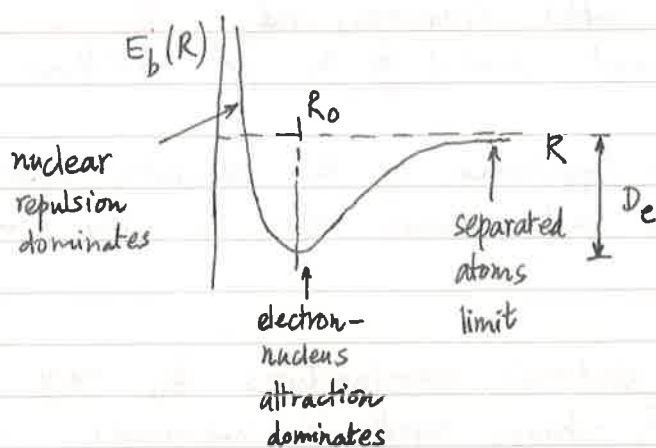
Since this is a set of uncoupled equations, we have, under the BO approximation the total molecular wavefunction

$$\Psi_b = F_b(\vec{R}) \Phi_b(\vec{R}; \{\vec{r}_i\})$$

Thus, in the BO approximation we first solve for the electronic wavefn assuming a fixed value of R .

The electronic energy eigenvalue E_b thus obtained then enters the decoupled nuclear motion wavefunction as a 'potential'

The general shape of the $E_b(R)$ function for a bound state is



$$D_e = E_b(\infty) - E_b(R_0)$$