

Course title: Quantum Chemistry-I
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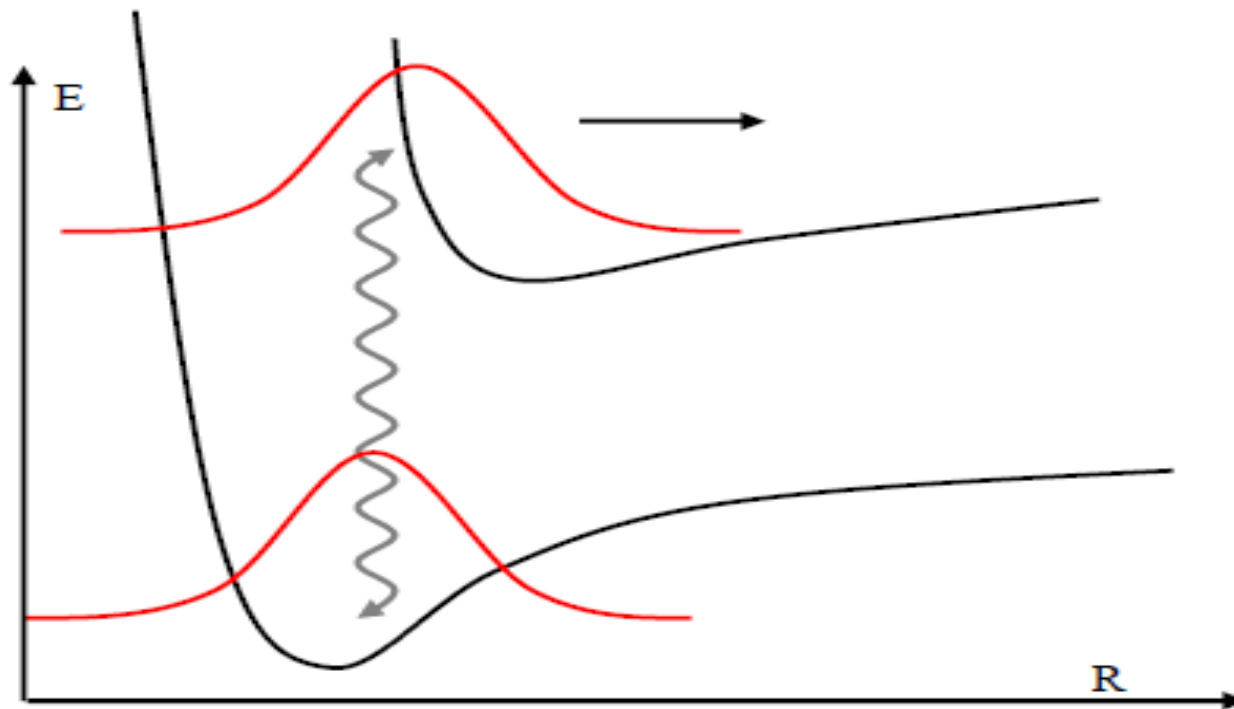
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TOPIC OF DISCUSSION

Born-Oppenheimer Approximations.

- In our next few classes we shall be discussing briefly about the preliminary idea of molecular quantum chemistry. Our aim is to develop a theory to solve the electronic time-independent Schrödinger equation. These theories are known as ab-initio (means from the 1st principal or from the beginning) quantum chemistry methods.
- we shall begin our discussion with one of the fundamental approximations of quantum chemistry , known as Born-Oppenheimer Approximations.

- The Born-Oppenheimer (BO) Approximation allows us to investigate the electronic structure of molecules very accurately without worrying about the nucleus. This theory forms a basis how most of the chemists think about molecule. Often you can find a picture shown in below for the electronic transition in spectroscopy, this picture is drawn on the basis of BO approximation.



- What is BO approximation?

In 1927, physicist Max Born and J. R. Oppenheimer suggested that as the nuclei are much heavier than the electrons in a molecular system, the electrons move much much faster than the nuclei and they react instantly to the nuclear change.

In other words nuclei remain effectively stationary or fixed with respect to the movement of electrons and hence their motion can be separated. The electron can be viewed as moving in the potential field of stationary nuclei.

For any molecule, we can write down the Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}},$$

Here i and j refer to the electron and A , B refer to the nuclei. In atomic units, Hamiltonian can be written as

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}}.$$

The Schrödinger equation may be written more compactly as:

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}),$$

Where \mathbf{R} is the set of nuclear coordinates and \mathbf{r} is the set of electronic coordinates. $T_N(\mathbf{R})$ and $T_e(\mathbf{r})$ represent nuclear and electronic K.E., V_{eN} is electron-nucleus attraction, $V_{NN}(\mathbf{R})$ and $V_{ee}(\mathbf{r})$ are nuclear-nuclear and electron-electron repulsion respectively. Here, the term $\hat{V}_{eN}(\mathbf{r}, \mathbf{R})$ prevent us from separating the Hamiltonian into nuclear and electronic parts.

- Here we introduce the BO approximation, which allows us to say that the nuclei are nearly stationary with respect to electron.

- We can separate the electronic and nuclear part.

- The total molecular wavefunction can be written as:

$$\Psi(\mathbf{r}; \mathbf{R})\chi(\mathbf{R}).$$

- The dependence of electronic wavefunction $\Psi(\mathbf{r}; \mathbf{R})$ on \mathbf{R} would be parametric and we can fix the nuclear coordinate \mathbf{R} at a certain value and solve for the electronic wavefunction which depends on \mathbf{R} only parametrically.

- And if we do this for a range of \mathbf{R} , we obtain the potential energy curve, along which nuclei move.

- This product wave function is known as Born-Oppenheimer wave function. The term $\chi(\mathbf{R})$ is the vibrational wave function, which is a function of nuclear coordinates \mathbf{R} and depends upon the vibrational and electronic quantum states.
- The electronic wave function is a function of both nuclear and electronic coordinates, but depends only on electronic state.
- Translational and rotational motions are not included here. If we simply multiply the translational and rotational wave functions with vibrational and electronic coordinate, we shall get the total molecular wave function, provided rotational and translational motions are not coupled with vibrational and electronic motion.

Now to calculate the electronic wave function, R is considered to be R_e , equilibrium separation of the nuclei and electronic wavefunctions are considered to be same for all positions of the nuclei.

We can neglect $T_N(R)$, since the mass of nucleus is much higher than the electronic mass, hence $T_N(R)$ becomes negligible. Thus for a fixed nuclear configuration, we have:

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

Such that
$$\hat{H}_{el}\Psi(\mathbf{r}; \mathbf{R}) = E_{el}\Psi(\mathbf{r}; \mathbf{R})$$

Now, as R becomes just a parameter, V_{NN} becomes a constant and shifts the eigen value by a constant number, hence we can also neglect V_{NN} .

The electronic Schrödinger equation becomes

$$\hat{H}_e \Psi(\mathbf{r}; \mathbf{R}) = E_e \Psi_e(\mathbf{r}; \mathbf{R})$$

Where,

$$\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

If spin-orbit (SO) interaction becomes important, then H_{SO} is to be included in Hamiltonian. So, we are not able to calculate the electronic wave function

Now the electronic energy E_{el} combines with the repulsive coulomb energy of two nuclei V_{NN} , to form the potential energy function that controls the nuclear motion

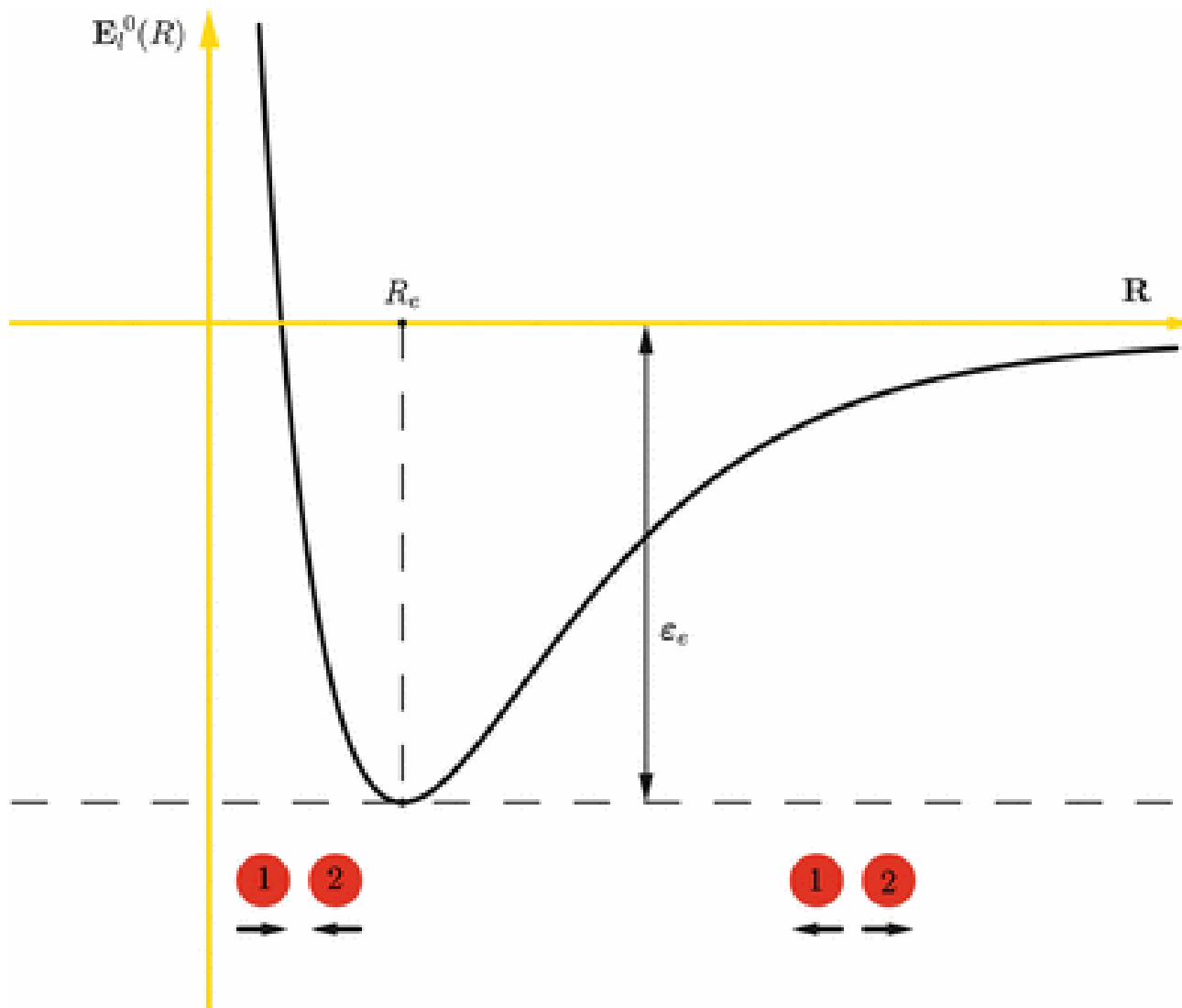
$$V_e(\mathbf{R}) = E_{el}(\mathbf{R}) + V_{NN}(\mathbf{R})$$

Consequently, the Schrödinger equation for the vibrational motion is

$$(T_N(\mathbf{R}) + V_e(\mathbf{R}))\chi(\mathbf{R}) = E_{ne}\chi(\mathbf{R})$$

Actually, the electronic Schrödinger equation is solved using BO approximation at a particular \mathbf{R} , to obtain the electronic wavefunctions and the potential energy $V_e(\mathbf{R})$.

The potential energy like,



So, from this curve we can conclude

- This is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function of the nuclei.
- When R is very large, the two molecules are weakly interacting.
- As R becomes smaller, the interaction (intermolecular attraction) become stronger (energy is large -ve) and the bond is formed.
- When the separation R becomes very small, the intermolecular repulsion is very large (energy is large +ve).

- The equilibrium position of the nuclei is where the function is a minimum (energy | minimum) i.e at $R=R_0$.
- While the potential energy function for a diatomic molecule is a curved line, the molecules with more than two atoms will have multidimensional potential energy surface, depending upon the numbers of internal degrees of freedom.
- The potential energy surface concept can be used to extract theoretically the **structures of molecule, finding its bond length, rates of chemical reactions** etc. It provides the idea about how potential energy varies with molecular motion for a given reaction or process.

Reference: Molecular Quantum mechanics, Atkins and Friedman, 4th edition, chapter:8

Questions Prepare yourself:

Explain the Born-Oppenheimer approximation..

Explain how can we obtain electronic wavefunction using Born-Oppenheimer approximation.

Explain: how can you calculate the potential energy curve fo diatomic molecule.

Write down the significance of potential energy diagram or potential energy surface.