

Week 9

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

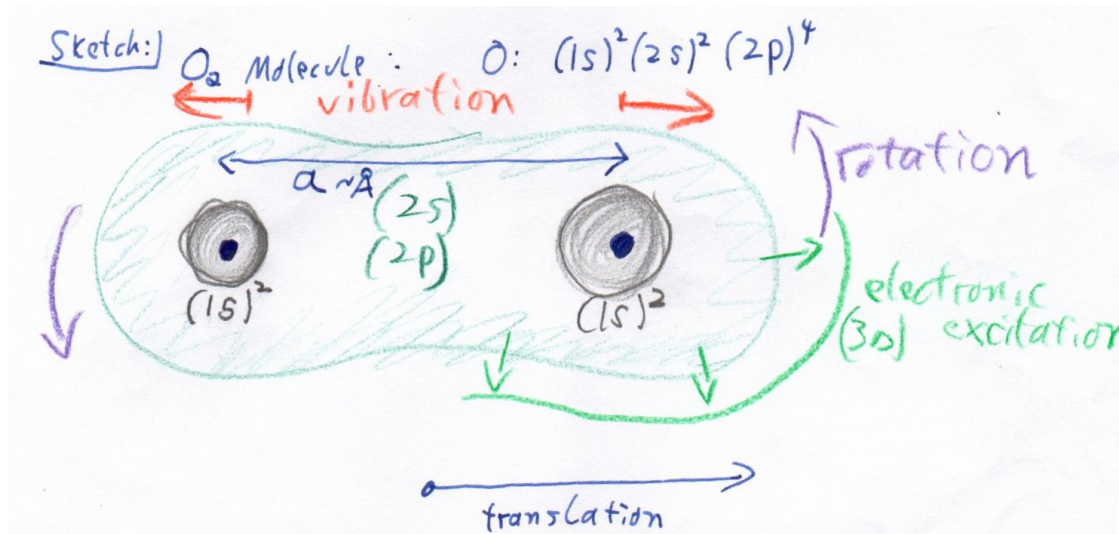
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4 Molecules

4.1 General Molecular Structure

- heavy atoms = one nucleus, many electrons
- molecule = at least two nuclei, many electrons

Complication: All e^- in an atom behave a bit "hydrogenic". No longer true in molecules.



From uncertainty relation, electronic energies $E_{elec} \sim \frac{\hbar^2}{ma_0^2} \sim eV$ as in atoms⁴. We shall see

$$\text{Vibrational energy} \quad E_{vib} \sim \left(\frac{m}{M}\right)^{\frac{1}{2}} E_{elec} \quad \text{Rotational energy} \quad E_{rot} \sim \left(\frac{m}{M}\right) E_{elec}$$

where, m = electron mass and M = nuclear mass (see Assignment 4, 2017).

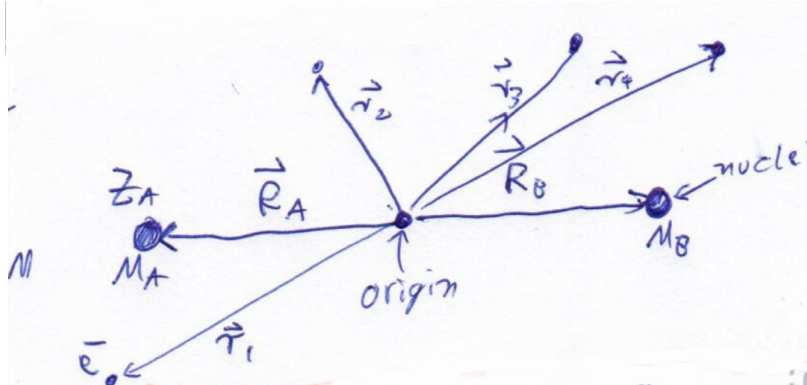
Since $\frac{m}{M} \ll 1$, we obtain the energy scale hierarchy $E_{elec} \gg E_{vib} \gg E_{rot}$. The fact that $\frac{m}{M} \ll 1$ also leads to the most essential approximation technique in molecular physics, see next section.

⁴Into $\Delta x \Delta p = \hbar$ insert $\Delta x \approx a_0$ (Bohr radius), then use $E_{elec} \approx \Delta p^2 / (2m)$

4.2 Born-Oppenheimer separation

We discuss di-atomic molecules to save notation, larger molecules can be treated the same. Consider N electrons

e.g., $N=4$



left: Sketch of co-ordinate system for generic di-atomic molecule. We choose the origin as the centre of mass of the nuclei A , B and employ the separation vector $\mathbf{R} = \mathbf{R}_B - \mathbf{R}_A$.

Molecular Schrödinger equation:

$$[\hat{T}_n + \hat{T}_e + \hat{V}]\psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (4.1)$$

$$\text{Nuclear Kinetic energy } \hat{T}_n = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2,$$

$$\text{where } \mu = \frac{M_A M_B}{M_A + M_B}$$

$$\text{Electron Kinetic energy } \hat{T}_e = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 \right)$$

Potential Energy

$$\hat{V} = -\sum_{i=1}^N \frac{Z_A e^2}{(4\pi\epsilon_0)|\mathbf{r}_i - \mathbf{R}_A|} - \sum_{i=1}^N \frac{Z_B e^2}{(4\pi\epsilon_0)|\mathbf{r}_i - \mathbf{R}_B|} + \sum_{\substack{i,j=1 \\ i < j}}^N \frac{e^2}{(4\pi\epsilon_0)|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z_A Z_B e^2}{(4\pi\epsilon_0)|\mathbf{R}|}$$

- Nuclei are $\sim \mathcal{O}(10^5)$ heavier than electrons. They move much slower. Hence, let's first consider an equation for electrons only.

Electronic Wave Equation / Schrödinger equation for the electrons *only*:

$$\underbrace{[\hat{T}_e + \hat{V}(\mathbf{R})]}_{\hat{H}_{el}} \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (4.2)$$

- Here, \mathbf{R} is just viewed as a parameter in the Hamiltonian, since there are no derivatives with respect to it. Thus Eq. (4.2) is not a PDE in terms of \mathbf{R} .
- Since \hat{H}_{el} depends parametrically on \mathbf{R} , so do its eigenfunctions and energies.
- These electronic wave functions are a complete orthonormal basis for each choice of $R \Rightarrow$

can write total wavefunction as

$$\Psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_q F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (4.3)$$

The $F_q(\mathbf{R})$ are called the nuclear wave function. Read them as: " $|F_q(\mathbf{R})|^2 d^3\mathbf{R}$ " is the probability to find the nuclei at \mathbf{R} when electrons are in the state q . Now, insert (4.3) into (4.1). We find (using (4.2)):

$$\sum_q \left\{ \hat{T}_n [F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)] + E_q(\mathbf{R}) F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) - E F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \right\} = 0. \quad (4.4)$$

In the first term (kinetic energy) $\nabla_{\mathbf{R}}^2$ acts on both $F_q(\mathbf{R})$ and $\Phi_q(\mathbf{R})$ so we need the product rule:

$$\hat{T}_n(F_q \Phi_q) = -\frac{\hbar^2}{2\mu} [(\nabla_{\mathbf{R}}^2 F_q) \phi_q + 2(\nabla_{\mathbf{R}} F_q \cdot \nabla_{\mathbf{R}} \phi_q) + F_q(\nabla_{\mathbf{R}}^2 \Phi_q)] \quad (4.5)$$

Finally we project (4.4) onto ϕ_s by performing the integration

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \phi_s^*(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \dots$$

on both sides of Eq. (4.4) \Rightarrow

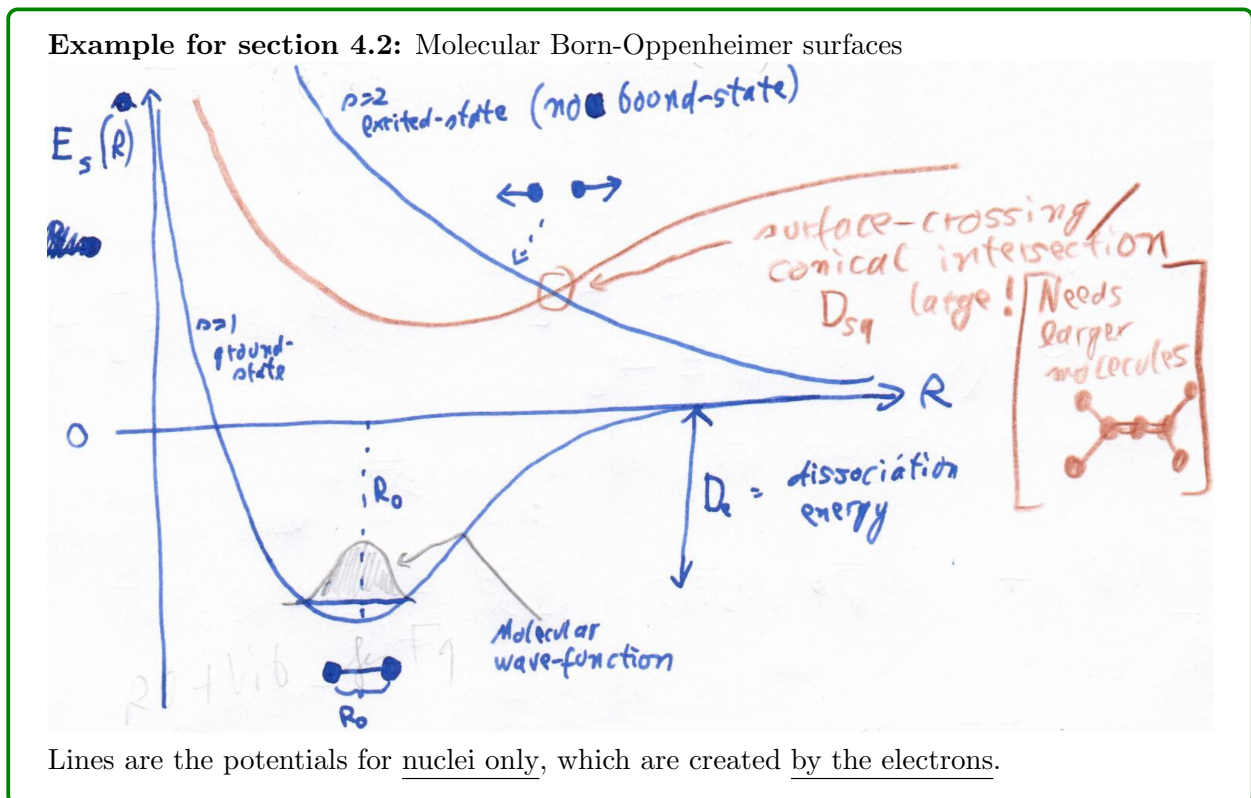
Molecular Schrödinger equation in Born-Oppenheimer separation

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 + E_S(\mathbf{R}) \right] F_S(\mathbf{R}) + \sum_q D_{sq}(\mathbf{R}) F_q(\mathbf{R}) = E F_S(\mathbf{R}) \quad (4.6)$$

where we use the non-adiabatic coupling operator,

$$D_{sq}(\mathbf{R}) = -\frac{\hbar^2}{2\mu} (\langle \phi_s | \nabla_{\mathbf{R}}^2 | \phi_q \rangle + 2\langle \phi_s | \nabla_{\mathbf{R}} | \phi_q \rangle \cdot \nabla_{\mathbf{R}} \dots) \quad (4.7)$$

- Eq. (4.6) is an exact rewriting of Eq. (4.1). As such it is equally hard to solve.
- However, we can frequently neglect all D_{sq} . This is called the Born-Oppenheimer approximation. This allows a separate treatment of the electrons and the nuclei and often the use of a single index "q".
- $E_S(R)$ is called a Born-Oppenheimer (potential energy) surface.
- BO approximation is often good since electrons are much lighter than nuclei $m_e \ll \mu$. It fails however, whenever $E_{s_1}(\mathbf{R}) = E_{s_2}(\mathbf{R})$ regardless of masses, which does happen in quite a lot of molecules.



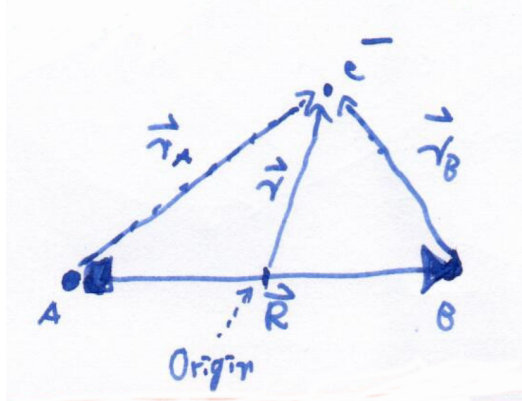
The next questions are now:

- Which nuclear energy surfaces $E_s(\mathbf{R})$ do we obtain from Eq. (4.2)?
 ↪ Electronic structure of molecules, see section 4.3.
- What dynamics can nuclei undergo on the surfaces $E_s(\mathbf{R})$?
 ↪ Molecular Rotations and vibrations, see section 4.6.

4.3 Electronic Structure of Molecules

We begin with the simplest molecule which is H_2^+ (Hydrogen molecular ion).

Diagram



At A, B we have the two protons (nuclei), with separation vector $\mathbf{R} = \mathbf{R}_B - \mathbf{R}_A$ as before.

H_2^+ Hamiltonian in atomic units: (to be used in the electronic SE (4.2))

$$\hat{H}_{el} = -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \quad \mathbf{r}_A = \mathbf{r} + \frac{\mathbf{R}}{2} \quad (4.8)$$

$$\mathbf{r}_B = \mathbf{r} - \frac{\mathbf{R}}{2}$$

We can first try to find eigen-states using Linear Combination of Atomic Orbitals (LCAO). Consider $R \rightarrow \infty$. Physically an electron near one of the nuclei should be in a hydrogen state, unperturbed by the far away other proton. Using the Hydrogen states from ϕ_{nlm} from Eq. (1.35) we can write this e.g. as

$$\phi(\mathbf{R}; \mathbf{r}) = \phi_{nlm}(\mathbf{r}_A) \cdot \quad (4.9)$$

see Eq. (4.2) e.g. $nlm \rightarrow 100$

The wave function (4.9) represents the electron attached to nucleus A only, unperturbed by the presence of far-away B . \Rightarrow However, recall our discussion of symmetries in the Helium Hamiltonian, section 2.3: There the wave-function had to be symmetric or antisymmetric under swap of the two electrons, because the Hamiltonian was symmetric under this swap.

Now, (4.8) is symmetric under $\mathbf{R}_A \leftrightarrow \mathbf{R}_B \Rightarrow \mathbf{r}_A \leftrightarrow \mathbf{r}_B$. So reasonable ground state wave-functions have to again be symmetric or anti-symmetric under the swap $\mathbf{R}_A \leftrightarrow \mathbf{R}_B$.

gerade (even) wavefunction (molecular orbital)

$$\phi_g(\mathbf{R}; \mathbf{r}) = \frac{1}{\sqrt{2}} (\phi_{1s}(\mathbf{r}_A) + \phi_{1s}(\mathbf{r}_B)) \quad (4.10)$$

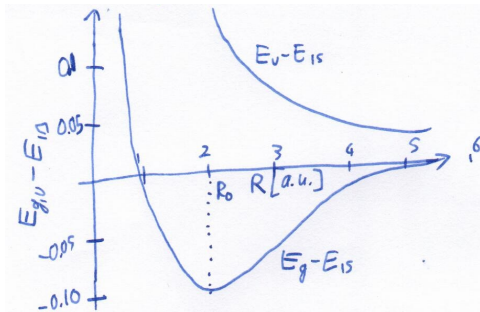
ungerade (odd) wavefunction

$$\phi_u(\mathbf{R}; \mathbf{r}) = \frac{1}{\sqrt{2}} (\phi_{1s}(\mathbf{r}_A) - \phi_{1s}(\mathbf{r}_B))$$

The reasoning above is strictly true for $R \rightarrow \infty$ only, but we can now use Eq. (4.10) as trial function for the variational principle (2.89). We can use that to get an upper bound on the ground-state energy of the molecule

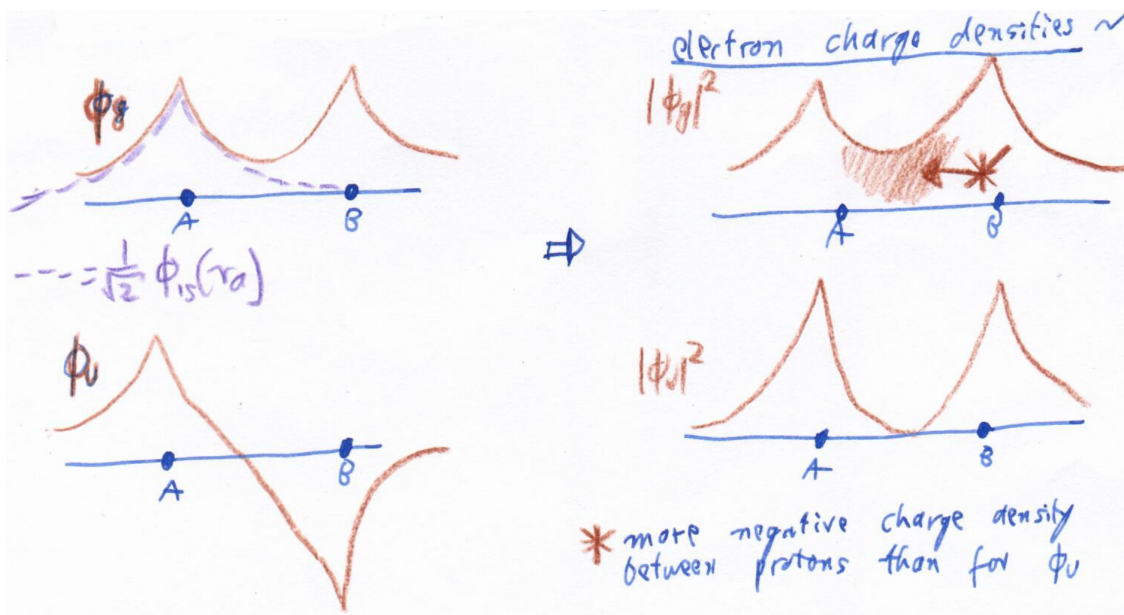
$$E_0 \leq E_{g,u}[R] \quad \text{where } E_{g,u}(R) = \frac{\langle \phi_{g,u} | \hat{H}_{se} | \phi_{g,u} \rangle}{\langle \phi_{g,u} | \phi_{g,u} \rangle} \quad (4.11)$$

Can evaluate the energy functional $E_{g,v(R)}$ (see text book), in particular now also taking into account the electron-electron repulsion in Eq. (4.8), which has been ignored in setting up the Ansatz (4.10). We get:



- ϕ_g is bonding
- ϕ_u is anti-bonding (repulsive)
- These are the lowest 2 molecular states, many more exist, based on $\phi_{2s}, \phi_{2p_1} \dots etc$

We can understand these two cases graphically, by drawing the states (their electron charge density):



It is apparent that in the bonding (gerade) state, electrons have an increased likelihood to be found exactly in between the nuclei. Their negative charge can then “glue” the two positive charges of the nuclei together.