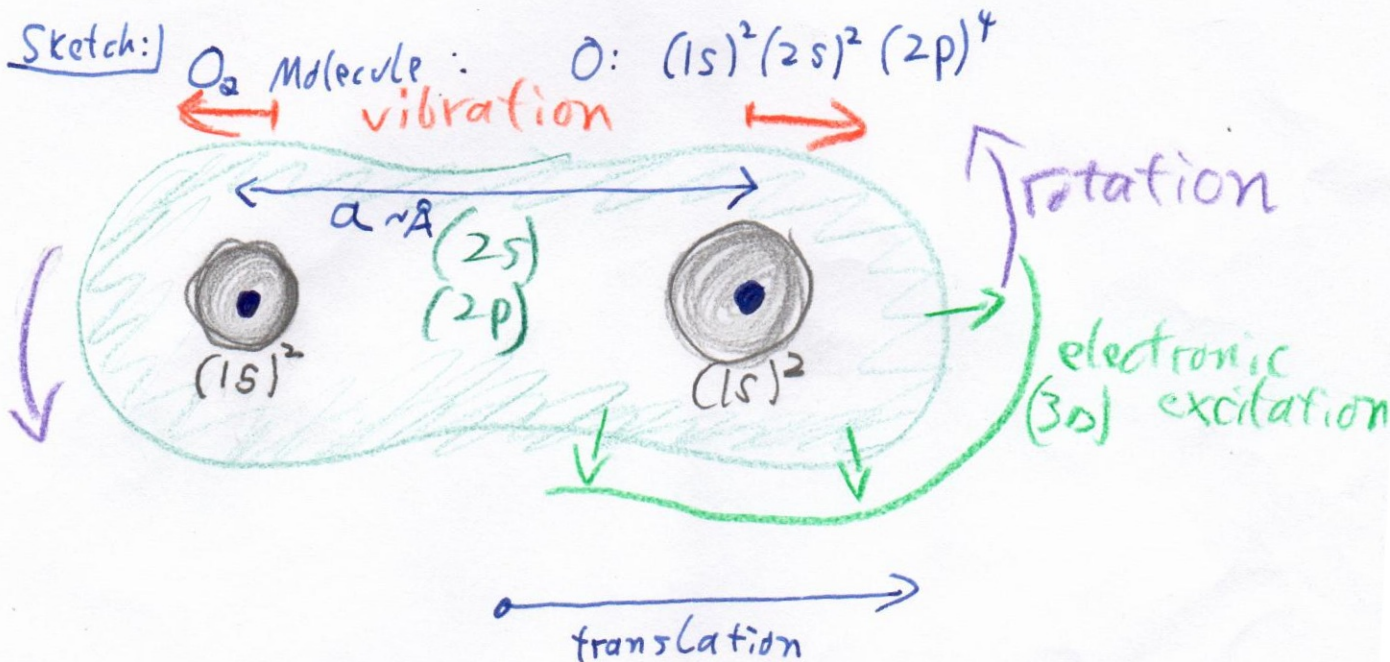


⑨ 4. MOLECULES

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 molecule:



From uncertainty relation, electronic energies $E_{elec} \sim \frac{\hbar^2}{ma^2} \sim eV$
as in atoms.

We shall see vibrational energy

(m = electron mass,
 M = nuclear mass)

$$E_{vib} \sim \left(\frac{m_e}{M}\right)^{1/2} E_{elec}$$

rotational energy

$$E_{rot} \sim \left(\frac{m_e}{M}\right)^2 E_{elec}$$

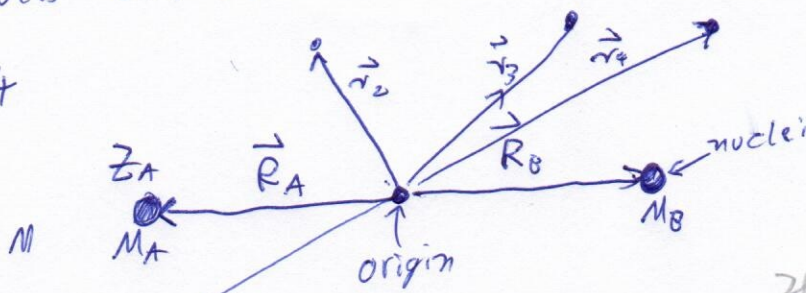
Since $\left(\frac{m_e}{M}\right) \ll 1$ $E_{elec} \gg E_{vib} \gg E_{rot}$.

The fact that $\frac{m_e}{M} \ll 1$ also leads to the most essential approximation technique in molecular physics, see next section

4.2. Born - Oppenheimer separation

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

eg $N=4$



Origin is C.M. of nuclei A, B

$$\vec{R} = \vec{R}_B - \vec{R}_A$$

If confused, think of one e^-
 H_2^+ (all same results)

Molecular Schrödinger equation:

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

Nuclear kinetic energy $\hat{T}_N = -\frac{\hbar^2}{2M} \nabla_{\vec{R}}^2$ $M = \frac{M_A M_B}{M_A + M_B}$

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

Potential energy

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

- Nuclei are $\sim \mathcal{O}(10^4)$ heavier than electrons. They move much slower. Hence let's first consider an equation for electrons only.

Electronic Wave-equation

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

Here \vec{R} is just viewed as a parameter in the Hamiltonian.

Since \hat{H}_e depends on \vec{R} , so do eigenfunctions and energies

these electronic wavefunctions are a complete orthonormal basis for each value of $\vec{R} \Rightarrow$

Can write total wavefunction as

$$\psi(\vec{R}; \vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) = \sum_q F_q(\vec{R}) \phi_q(\vec{R}; \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad (4.3)$$

The $F_q(\vec{R})$ are called nuclear wavefunction.

Read them as " $|F_q(\vec{R})|^2 d\vec{R}$ " in the probability to find nuclei at \vec{R} when electrons are in state q .

Now insert (4.3) into (4.1). We find (using (4.2))

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

In the first term $\vec{\nabla}_R$ acts on both, F_q and Φ_q , so we need the ~~product~~ product rule:

$$\hat{T}_N(F_q \Phi_q) = -\frac{\hbar^2}{2\mu} \left[F_q (\vec{\nabla}_R^2 \Phi_q) + 2(\vec{\nabla}_R \cdot F_q) \cdot \vec{\nabla}_R \Phi_q + \Phi_q (\vec{\nabla}_R^2 F_q) \right] \quad (4.5)$$

Finally we project (4.4) onto Φ_0 by doing

$\int d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N \Phi_0^*(\vec{R}; \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \dots$
on both sides \Rightarrow

Molecular Schrödinger equation in Born-Oppenheimer separation:

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

where we use non-adiabatic coupling (operators)

$$D_{sq}(\vec{R}) = -\frac{\hbar^2}{2\mu} \left(\langle \Phi_0 | \vec{\nabla}_R^2 | \Phi_q \rangle + 2 \langle \Phi_0 | \vec{\nabla}_R | \Phi_q \rangle \cdot \vec{\nabla}_R \dots \right) \quad (4.7)$$

• Eq. (4.6) is an exact rewriting of (4.1). As such it is equally hard to solve.

• We can frequently neglect all D_{sq} in the Born-Oppenheimer approximation. This allows a separate treatment of electrons & nuclei and often the use of a single "q".

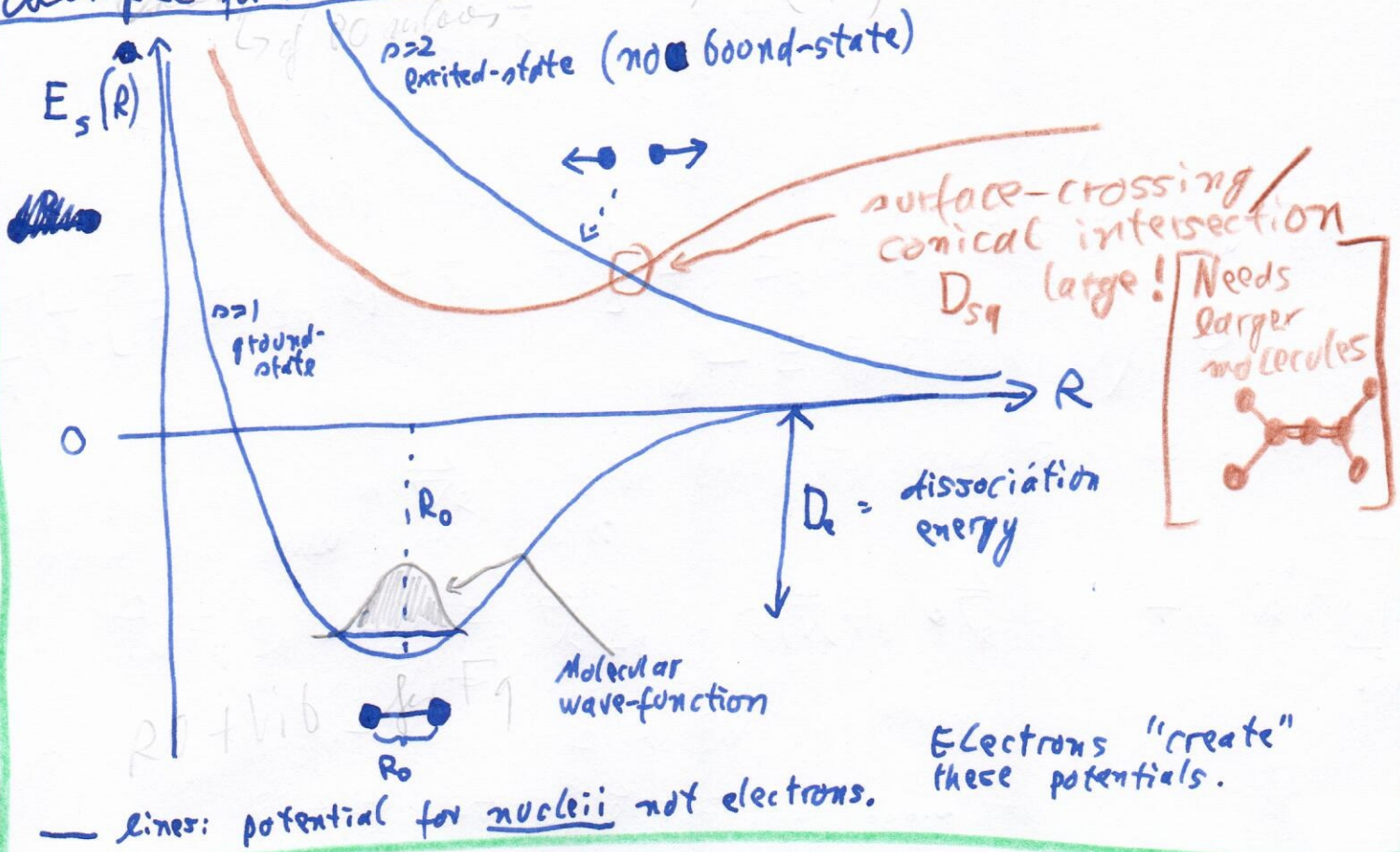
• $E_S(\vec{R})$ is called a Born-Oppenheimer (potential energy) surface

• BO-approximation is often good due to $m_e \ll \mu$.

It fails however, when $E_{S_1}(\vec{R}) = E_{S_2}(\vec{R})$, which does happen.

⊙

Example for section 4.2 | Molecular Born-Oppenheimer surfaces:



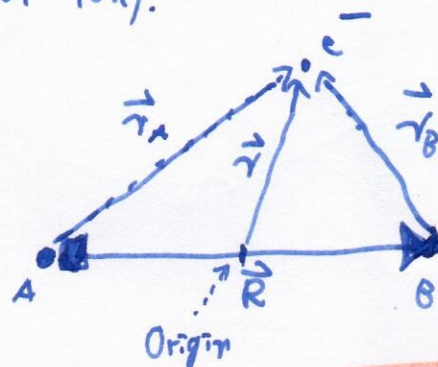
Next questions now:

- which $E_s(R)$ do we obtain from (4.2)
 - ↳ Electronic structure (4.3), (4.4)
- what dynamics can nuclei undergo on the surfaces $E_s(R)$
 - ↳ Molecular rotations and vibrations (4.5)

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)

$$\vec{R} = \vec{R}_B - \vec{R}_A$$

The H_2^+ Hamiltonian in atomic units:] (for equation (4.2))

$$\hat{H}_{ee} = -\frac{1}{2} \nabla_{\vec{r}}^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

$$\begin{aligned} \vec{r}_A &= \vec{r} + \frac{1}{2}\vec{R} \\ \vec{r}_B &= \vec{r} - \frac{1}{2}\vec{R} \end{aligned}$$

(4.8)

Solve this 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:

$$\text{e.g. } \Phi(\vec{R}_i; \vec{r}) = \phi_{n\ell m}(\vec{r}_A)$$

↑
↑
re Eq. (4.2)
e.g. 100

with $\phi_{n\ell m}$ from (1.18)

However, recall our discussion of symmetries in the helium Hamiltonian: (section 2.3.1). There the wavefunction 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 $\vec{R}_A \leftrightarrow \vec{R}_B \Rightarrow \vec{r}_A \leftrightarrow \vec{r}_B$. So reasonable ground-state wave-functions are

gerade (even) wavefunction (molecular orbital)

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

(4.9)

ungerade (odd) wavefunction

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

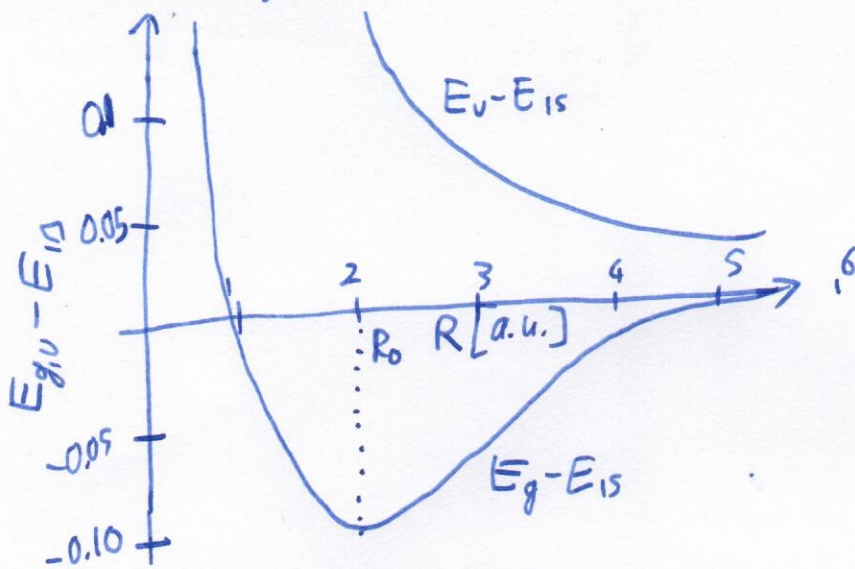
The reasoning above is true for $R \rightarrow \infty$, but can use Eq (4.9) as trial function for the Variational principle (2.32)

Thus ground-state energy of molecule

$$E_0 \leq E_{g_0}[R] \quad \text{where} \quad E_{g_0}(R) = \frac{\langle \phi_{g_0}(R) | \hat{H}_{el} | \phi_{g_0}(R) \rangle}{\langle \phi_{g_0}(R) | \phi_{g_0}(R) \rangle}$$

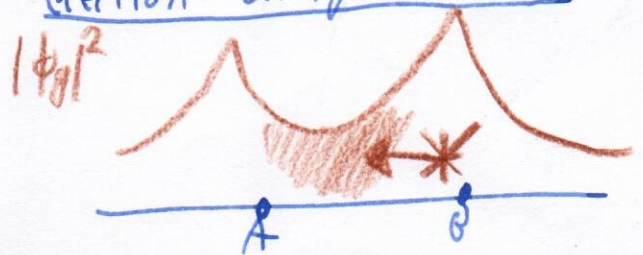
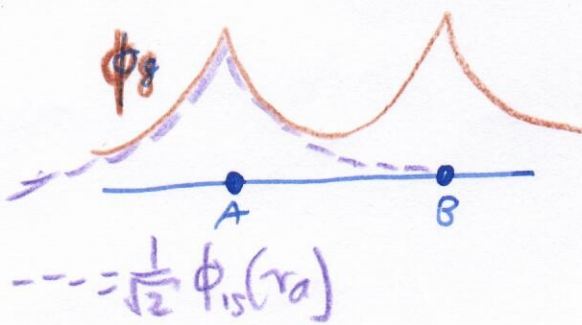
↑
some parameter

Can evaluate $E_{g_0}(R)$ (see text book), and get:

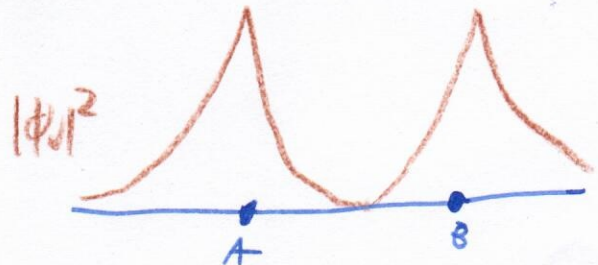
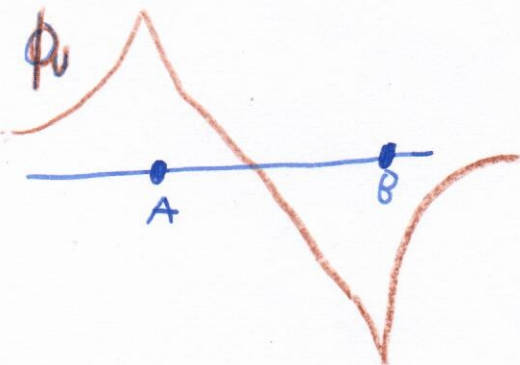


- ϕ_g is bonding
- ϕ_u is anti-bonding (repulsive)
- these are the lowest 2 molecular states, many more exist, based on $\phi_{2s}, \phi_{2p}, \dots$ etc.

We can understand these two cases graphically, by drawing the state electron charge densities \sim



\Rightarrow



* more negative charge density between protons than for ϕ_u