

Course 2

1. Atomic units
2. Basic concepts
3. Born-Oppenheimer approximation

1. Atomic Units

$$m_e=1, e=1, a_0=1, h = 2\pi, e^2/4\pi\epsilon_0 a_0 = 1$$

Symbol	Quantity	Value in a.u.	Value in SI units
m_e	Mass (Electron mass)	1	$9.1094 \cdot 10^{-31} \text{Kg}$
e	Charge (Electron charge)	1	$1.6022 \cdot 10^{-19} \text{C}$
a_0	Length (Bohr first radius ($\hbar^2/(kme^2)$))	1	$0.52918 \cdot 10^{-10} \text{m}$
E_H	Energy ($E_H = \hbar^2/m_e a_0^2$)	1	$27.2114 \text{eV} = 4.3597 \cdot 10^{-18} \text{J}$
\hbar	Angular momentum	1	$1.0546 \cdot 10^{-34} \text{Js}$
v_B	Velocity ($\alpha \cdot c = e^2/4\pi\epsilon_0 \hbar$)	1	$2.187691 \cdot 10^6 \text{m} \cdot \text{s}^{-1}$
τ_0	Time ($\tau_0 = \hbar/E_H$)	1	$2.418884 \cdot 10^{-17} \text{s}$
$4\pi\epsilon_0$	Vacuum permittivity	1	$1.113 \cdot 10^{-10} \text{C}^2/(\text{Jm})$
d_0	Electric dipole moment (ea_0)	1	$8.478 \cdot 10^{-30} \text{Cm}$
$e^2 a_0^2 E_H^{-1}$	Electric polarizability	1	$1.649 \cdot 10^{-41} \text{C}^2 \text{m}^2 \text{J}^{-1}$
Derived units			
h	Planck's constant	2π	$6.626 \cdot 10^{-34} \text{Js}$
c	Speed of light ($c = v_B/\alpha$)	137.036	$2.998 \cdot 10^8 \text{m/s}$
μ_B	Bohr magneton ($e \hbar / 2m_e$)	$1/2$	$9.274 \cdot 10^{-24} \text{J/T}$
μ_N	Nuclear magneton	$2.723 \cdot 10^{-4}$	$5.051 \cdot 10^{-27} \text{J/T}$
μ_0	Vacuum permeability ($4\pi/c^2$)	$6.629 \cdot 10^{-4}$	$4\pi \cdot 10^{-7} \text{Js}^2/(\text{mC}^2)$
E_0	Electric field strength	1	$5.1423 \cdot 10^{11} \text{V/m}$

$$m_{\text{proton}} = 1836.15 \text{ au} \quad (1.6726 \times 10^{-27} \text{ kg})$$

$$\text{Energy: } 1 \text{ a.u.} = 27.212 \text{ eV} = 627.51 \text{ Kcal/mol} = 219470 \text{ cm}^{-1} \quad 1 \text{ Kcal/mol} = 4.184 \text{ KJ/mol}$$

$$\text{Electric dipole moment: } 1e a_0 = 2.54181 \text{ De}; 1D_e = 0.3934e a_0$$

Other fundamental constants:

$$\text{Boltzmann's constant: } k_B = 1.38066 \cdot 10^{-23} \text{ J/K}$$

$$\text{Avogadro's number: } N_A = 6.02205 \cdot 10^{23} \text{ mol}^{-1}$$

$$\text{Rydberg constant: } R_\infty = 1.097373 \cdot 10^7 \text{ m}^{-1}$$

$$\text{Compton wavelength of electron: } \lambda_C = 2.426309 \cdot 10^{-12} \text{ m}$$

$$\text{Stefan-Boltzmann constant: } \sigma = 5.67032 \cdot 10^{-8} \text{ W/(m}^2\text{K}^4)$$

Electric field unit:

Field=X+a => an electric field of **a*10⁻⁴ a.u.** is applied along the X direction.

$$1 \text{ a.u.} = \text{Hartree}/(\text{charge} \cdot \text{bohr}) = 27.2114 \cdot 1.6 \cdot 10^{-19} \text{ J}/(1.6 \cdot 10^{-19} \text{ C} \cdot 5.29177 \cdot 10^{-11} \text{ m})$$

$$1 \text{ a.u.} = 5.1423 \cdot 10^{11} \text{ V/m}$$

$$1 \text{ a.u.} = 51.423 \text{ V/\AA}$$

$$E_f(\text{V/\AA}) = 51.423 E_f(\text{a.u.})$$

Field=X+1000 means a field of 0.1 a.u. (5.1423 V/\AA) is applied along the X direction

For UV-Vis spectra:

$$E(\text{eV}) = \text{const.}/\lambda(\text{nm}) \approx \mathbf{1240}/\lambda(\text{nm}). \quad \lambda(\text{nm}) \approx 1240/E(\text{eV}) \\ = \mathbf{1239.9785}/\lambda(\text{nm})$$

Energy conversion factors

	Hartree (a.u.)	KJ/mol	Kcal/mol	eV	cm ⁻¹
Hartree (a.u.)	1	2625.5	627.51	27.2114	219470
KJ/mol	0.00038088	1	0.23901	0.010364	83.593
Kcal/mol	0.0015936	4.184	1	0.043363	349.75
eV	0.036749	96.485	23.061	1	8065.5
cm ⁻¹	4.5563E-06	0.011963	0.0028591	0.00012398	1

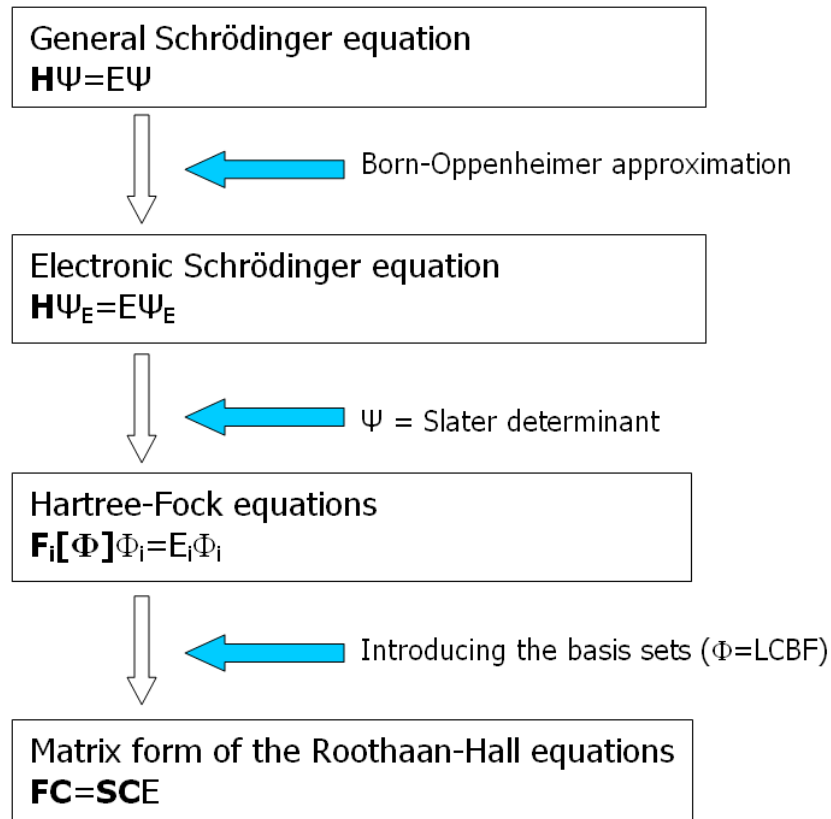
Hamiltonian for the hydrogen atom:

SI units:
$$-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

Atomic units:
$$-\frac{1}{2} \nabla^2 - \frac{1}{r}$$

2. Basic concepts

- molecular Hamiltonian
- form of many-electron wave-functions
(Slater determinants (SD) and linear combinations of SD)
- Hartree-Fock (HF) approximation
- more sophisticated approaches which use the HF method as a starting point
(correlated post-Hartree Fock methods)

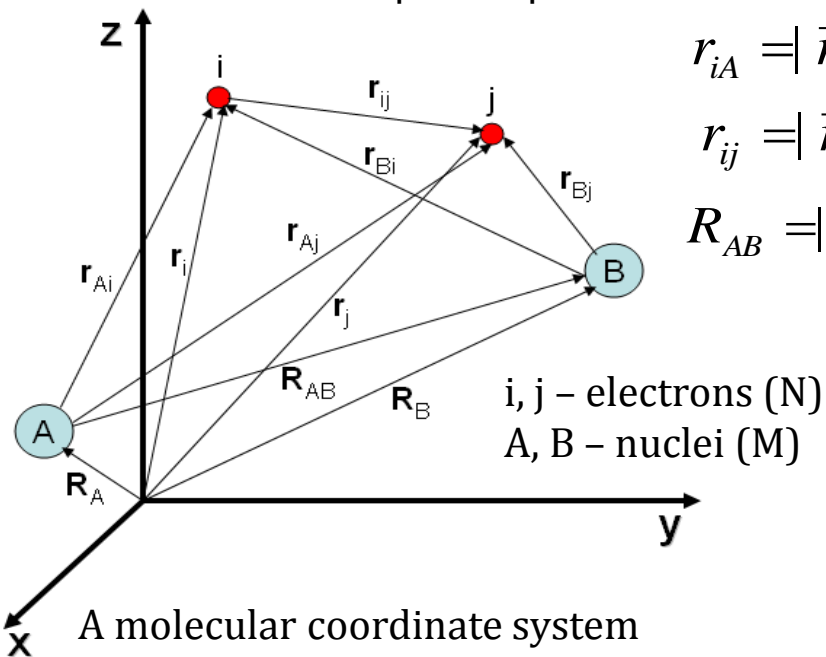


Approximations made in the framework of the
Hartree-Fock-Roothaan-Hall theory

The Molecular Hamiltonian

The non-relativistic time-independent Schrödinger equation:

$$\mathbf{H}|\Psi\rangle = E|\Psi\rangle$$



$$r_{iA} = |\vec{r}_{iA}| = |\vec{r}_i - \vec{R}_A|$$

$$r_{ij} = |\vec{r}_{ij}| = |\vec{r}_i - \vec{r}_j|$$

$$R_{AB} = |\vec{R}_{AB}| = |\vec{R}_A - \vec{R}_B|$$



$$\mathbf{H} = \underbrace{-\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{T_e} - \underbrace{\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2}_{T_N} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}}_{V_{NN}} \quad (1)$$

M_A - the ratio of the mass of nucleus A to the mass of an electron

Z_A - the atomic number of nucleus A

T_e - the operator for the kinetic energy of the electrons

T_N - the operator for the kinetic energy of the nuclei

V_{eN} - the operator for the Coulomb attraction between electrons and nuclei

V_{ee} - the operator for the repulsion between electrons

V_{NN} - the operator for the repulsion between nuclei

$$\nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$$

$$H = \underbrace{-\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{T_e} - \underbrace{\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2}_{T_N} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}}_{V_{NN}} \quad (1)$$

- represents the general problem

Exact solution for systems containing more than one electron is unknown!

-> approximations, approximations, ...

→ (1) must to be separated in two parts: **electronic** and **nuclear** problems

Born-Oppenheimer Approximation

$$\Psi = \Psi(x_1, \dots, x_N, X_1, \dots, X_M)$$

The term V_{eN} in the Hamiltonian prevents any wave-function $\Psi(\mathbf{x}, \mathbf{X})$ from being written as a product of an electronic and a nuclear wavefunction.

Thus, we need approximations so that we can factorize the wavefunction!

Assumptions:

The nuclei are much heavier than electrons ($m_{\text{proton}} = 1836m_e$)

→ they move much more slowly

→ can be considered frozen in a single arrangement (**molecular conformation**)

→ the electrons can respond almost instantaneously

to any change in the nuclear position



The electrons in a molecule are moving in the field of fixed nuclei.



$$\Psi = \Psi_e(\mathbf{x}, \{\mathbf{R}\}) \cdot \Psi_N(\mathbf{R})$$

- factorized (separable) form



$$H = \underbrace{-\sum_{i=1}^N \frac{1}{2} \nabla_i^2}_{T_e} - \underbrace{\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2}_{T_N} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}}_{V_{eN}} + \underbrace{\sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{r_{ij}}}_{V_{ee}} + \underbrace{\sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}}_{V_{NN}}$$

neglected

constant term

- Ψ_e is parametrically dependent on the positions of the nuclei ($\{\mathbf{R}\}$)
- SE is separated in 2 SEs, one for electrons and one for nuclei



two Hamiltonians

Assumption: For each value of the nuclear positions, the electronic system is in the electronic ground state, corresponding to the lowest $E_e(\mathbf{R})$.

Electronic Hamiltonian:

➤ describes the motion of N electrons in the field of M fixed point charges (nuclei)

$$H_e(\mathbf{R}) = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{r_{ij}} \quad (2)$$

$H_e(\mathbf{R})$ means that H_e depends on the nuclei positions (\mathbf{R} coordinate does not appear in H_e but r_{iA})

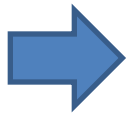
Electronic Schrödinger equation:

$$H_e(\mathbf{R})\Psi_e(\mathbf{x};\mathbf{R}) = E_e(\mathbf{R})\Psi_e(\mathbf{x};\mathbf{R}) \quad (3)$$

$$\Psi_e = \Psi_e(\mathbf{x};\mathbf{R}) \quad (4)$$

- the electronic wave-function which describes the motion of the electrons
- describes electronic states for fixed nuclear coordinates $\{\mathbf{R}\}$
- explicitly depends on the electronic coordinates
- parametrically depends on the nuclear coordinates because H is a function of the positions \mathbf{R} of the nuclei
- a different electronic wave-function is obtained for each nuclear configuration

$$E_e = E_e(\mathbf{R}) \quad (5)$$



Total energy:

$$E_{\text{tot}}^{\text{pot}}(\mathbf{R}) = E_e + \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (6)$$

Equations (2) - (6) $\equiv H_e(\mathbf{R}), \Psi_e, E_e$
= **electronic problem**

The **geometry dependent electronic energy**

- plays the role of the potential energy in the Schrodinger equation for the nuclear motion
- it is generally termed **potential energy surface (PES)**.

Potential energy surface (PES) examples

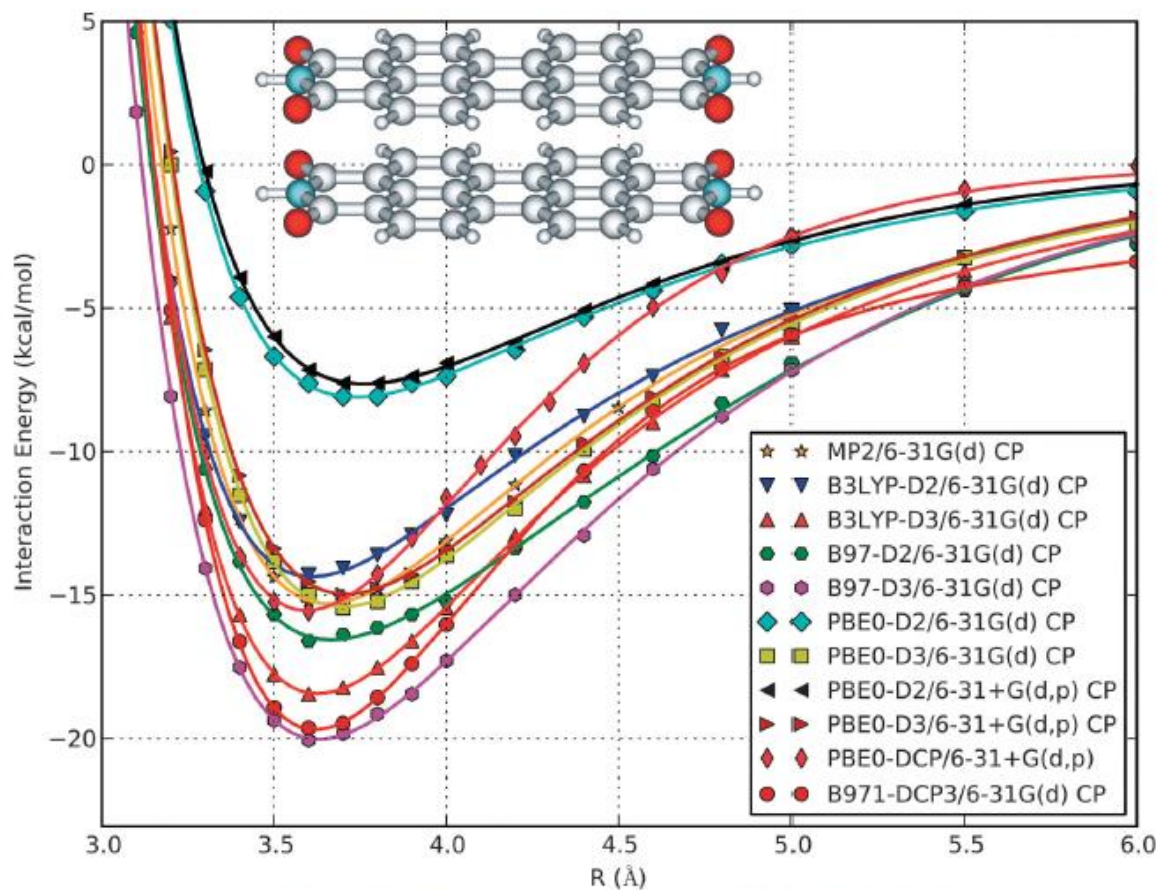


Fig. 1 Calculated potential energy curves for the stacked PTCDI dimer at different levels of theory, fitted to a Murrell-Sorbie potential function.

M. Oltean et al., *Phys. Chem. Chem. Phys.*, 15 (2013) 13978-13990

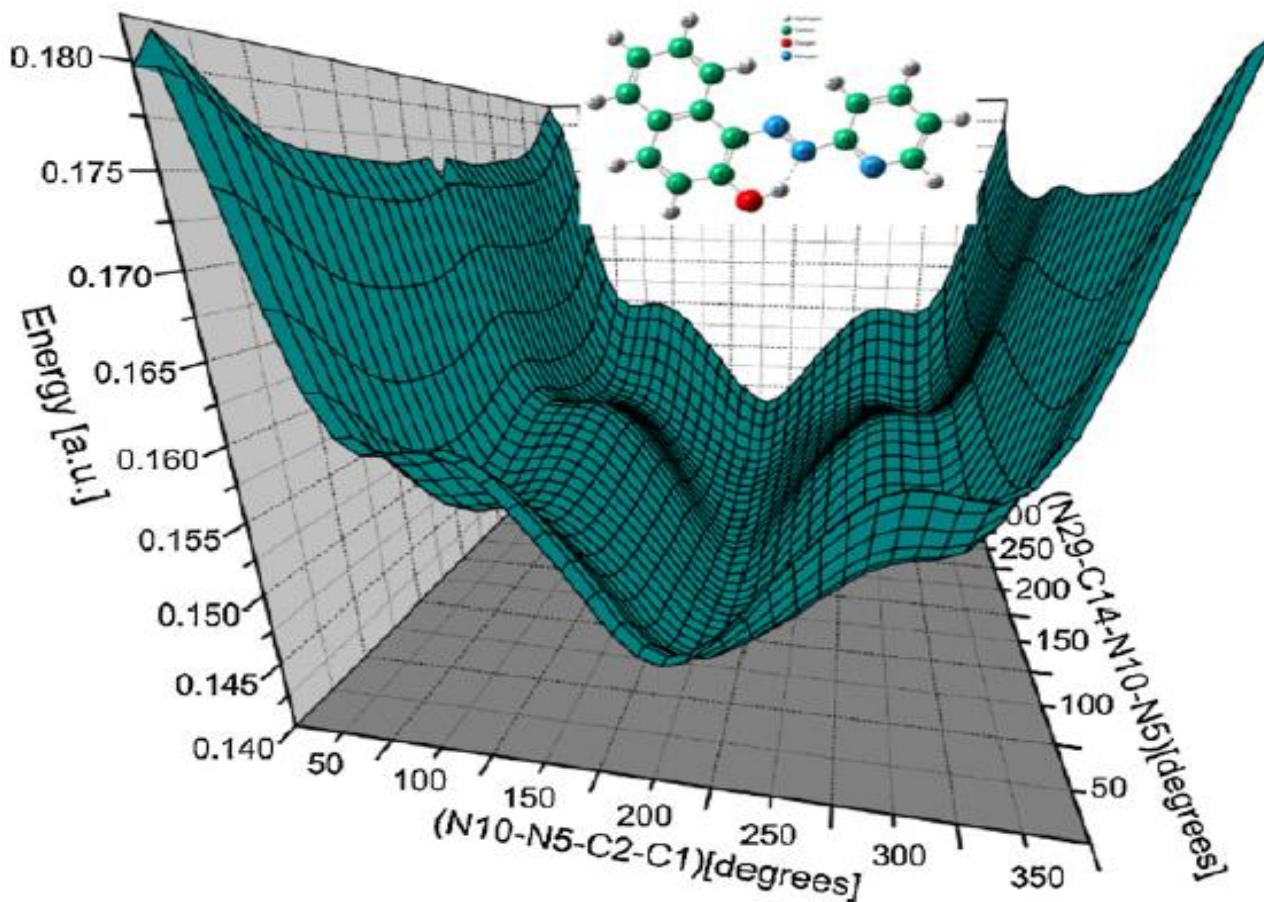


Fig. 2. PES of PAN scanned at PM6 level of theory.

L. Szabó et al. / Spectrochimica Acta Part A 93 (2012) 266–273

If the electronic problem is solved

- ▶ we can solve for the motion of the nuclei using the electronic energy $E(\mathbf{R})$ as the potential energy in Schrödinger equation for the nuclear motion.

Since the electrons move much faster than the nuclei

- ▶ we can replace the electronic coordinates by their average values (averaged over the electronic wave-function)

Nuclear Hamiltonian

- describes the motion of the nuclei **in the average field of the electrons**

$$\begin{aligned} H_N &= -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \left\langle -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{r_{ij}} \right\rangle + \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \\ &= -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + E_e(\{\mathbf{R}\}) + \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \\ &= -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + E_{tot}^{pot}(\{\mathbf{R}\}) \end{aligned}$$

or:

$$H_N = -\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \int_r \Psi(r, R) H_{elec} \Psi(r, R) dr + \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

- the integral corresponds to the potential energy of nuclei in the field of electrons.

Nuclear Schrödinger equation

$$H_N |\Psi_N\rangle = E |\Psi_N\rangle$$

Ψ_N

- nuclear wavefunction
- solution of the ro-vibrational problem for the nuclear coordinates, in the presence of an electronic potential energy surface
- describes the vibration, rotation and translation of a molecule

E

- **total energy of the molecule** (in the Born-Oppenheimer approximation)
- includes:
 - electronic energy
 - vibrational energy
 - rotational energy
 - translational energy

Total wave-function in the Born-Oppenheimer approximation:

$$\Psi(x, R) = \Psi_e(x, \{R\}) \cdot \Psi_N(R)$$

Born-Oppenheimer approximation

- usually a good approximation
- bad approximation for:
 - excited states (high energy for the nuclear motion)
 - degenerate or cuasidegenerate states

Requirements for the wave function

we assume the Born-Oppenheimer approximation and will only be concerned with the electronic Schrödinger equation.

1. Normalization

Ψ is normalized to unity:

$$\int \Psi^*(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r} = 1$$

Integration is performed over the coordinates of all N electrons.
The wavefunction must also be single-valued, continuous and finite.

2. Antisymmetry with respect to the permutation of two electrons

Electrons are fermions \rightarrow the electron **wave-function must be antisymmetric** with respect to the interchange of the coordinate \mathbf{x} (both space and spin) of any two electrons.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N)$$

3. The electronic wavefunctions must be eigenfunctions of S_z and S^2 operators

The electronic Hamiltonian

- does not contain any spin operators

- it commutes with the operators S_z and S^2 $[H, S_z]=0$ $[H, S^2]=0$

corresponding eigenvalues: M_S and $S(S+1)$, respectively.

$$S_z = \sum_i^N s_{z_i} \rightarrow M_S \quad S^2 = \sum_i^N s_i^2 \rightarrow S(S+1)$$

We take care of spin by using spin-orbitals instead of pure spatial orbitals.

$\alpha(\sigma)$ and $\beta(\sigma)$ – spin functions (complete and orthonormal)

$$\int \alpha(\sigma)\alpha(\sigma)d\sigma = \int \beta(\sigma)\beta(\sigma)d\sigma = 1$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

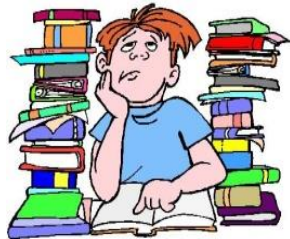
and

$$\int \alpha(\sigma)\beta(\sigma)d\sigma = \int \beta(\sigma)\alpha(\sigma)d\sigma = 0$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

The electrons are described by a set of spatial (\mathbf{r}) and spin (σ) coordinates:

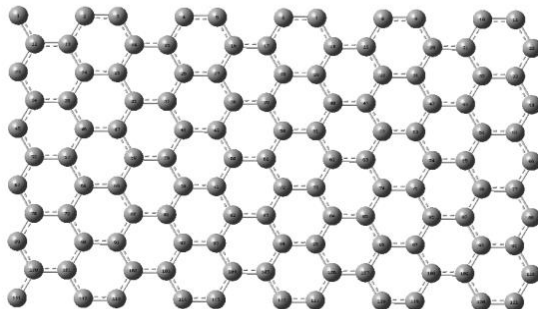
$$\mathbf{x} = \{\mathbf{r}, \sigma\}$$



Homework

Write a C program to calculate the coordinates of the atoms in a graphene sheet (10 x 10 atoms) whose structure is given below.

The C-C bond length in graphene is 1.42 Å.



The Nobel prize in physics for 2010 was awarded to Andre Geim and Konstantin Novoselov at the University of Manchester "for groundbreaking experiments regarding the two-dimensional material graphene".

Deadline: April 9-th, 2015