Lecture 3

Electronic wavefunctions and electronic density

C.-K. Skylaris
The Born-Oppenheimer approximation

• Nuclei are much heavier than electrons and move at much slower speeds
• For example, the nuclei in H\textsubscript{2} move only about 1pm for each 1000pm of electronic motion
• To a very good approximation, we can assume that the electronic motions are instantaneously “equilibrated” at each nuclear position

Example: Vibration of diatomic molecule:

Wrong picture: “electron cloud” trails behind moving nuclei

Correct picture: “electron cloud” instantaneously re-arranges itself around moving nuclei
Born-Oppenheimer approximation

For a molecule, the wavefunction is a function of the coordinates of all the electrons and all the nuclei:

\[ \Psi(r_1, r_2, \ldots, r_{N_{\text{electrons}}}, R_1, R_2, \ldots, R_{N_{\text{atoms}}}) \]

- The Born-Oppenheimer approximation is based on the fact that nuclei have much larger masses than the electrons
- To a good approximation, one can solve the Schrödinger equation only for the electrons and assume the nuclei are frozen
- We will use this approximation from now on
- As a result, our wavefunctions will be functions only of electronic coordinates:

\[ \Psi(r_1, r_2, \ldots, r_{N_{\text{electrons}}}) \]
The Born-Oppenheimer approximation

• In the Born-Oppenheimer approximation the nuclei are held fixed at given locations and we solve the Schrödinger equation for the wavefunction of the electrons alone
• The resulting molecular electronic energy depends on the nuclear coordinates
• For a diatomic we obtain the molecular potential energy curve
• For a polyatomic molecule we obtain the potential energy surface

Example: Potential energy curve of a diatomic

\[ E_{PES}(d) \]

Equilibrium geometry \( d_e \)

Internuclear Separation

\( \text{UNIVERSITY OF Southampton}
\]

School of Chemistry

CHEM6085 Density Functional Theory
Hamiltonian operator for water molecule

Water contains 10 electrons and 3 nuclei. We will use the symbols “O” for the oxygen (atomic number $Z_O=8$) nucleus, “H1” and “H2” (atomic numbers $Z_{H1}=1$ and $Z_{H2}=1$) for the hydrogen nuclei.

$$\hat{H}_{H_2O} = -\frac{1}{2M_O} \nabla^2 R_O - \frac{1}{2M_{H1}} \nabla^2 R_{H1} - \frac{1}{2M_{H2}} \nabla^2 R_{H2} - \sum_{i=1}^{10} \frac{1}{2} \nabla^2 r_i$$

- Kinetic energy of O
- Kinetic energy of H1
- Kinetic energy of H2
- Kinetic energy of electron $i$

$$- \sum_{i=1}^{10} \frac{1}{8} |r_i - R_O| - \sum_{i=1}^{10} \frac{1}{|r_i - R_{H1}|} - \sum_{i=1}^{10} \frac{1}{|r_i - R_{H2}|}$$

- Electron attraction to O
- Electron attraction to H1
- Electron attraction to H2

$$+ \sum_{i=1}^{10} \sum_{j=i+1}^{10} \frac{1}{|r_i - r_j|} + \sum_{I=1}^{3} \sum_{J=I+1}^{3} \frac{Z_I Z_J}{|R_I - R_J|}$$

- Electron-electron repulsion
- Nucleus-nucleus repulsion

E.g. Assume $Z_1 = Z_O$
$Z_2 = Z_{H1}$
$Z_3 = Z_{H2}$

• Quite a complicated expression! Hamiltonians for molecules become intractable
• Fortunately, we do not need to write all this for every molecule we study. We can develop general, much more compact expressions that apply to any molecule, irrespective of its size.
Example: Nuclear attraction potential for one O and two H

- How does the Hamiltonian operator differ between these examples?
- Can you suggest how you may model the reaction OH+H \rightarrow H_2O
Electronic wavefunctions

• Solutions (eigenfunctions) of the electronic Schrödinger equation (i.e. under the Born-Oppenheimer approximation)

• Electronic wavefunctions, whether exact or approximate, must have the following properties:
  • Be finite
  • Be continuous
  • Be single valued
  • Respect the indistinguishability of electrons
  • Their square modulus is a probability distribution
  • They must be antisymmetric
Continuous

good

bad
Single valued

good

bad
Spin

• Each electron has a “spin”, an intrinsic property which has the characteristics of rotational motion, and is quantised

• Electronic spin is described by a spin angular momentum quantum number $s=\frac{1}{2}$, and its $z$-component $m_s = \frac{1}{2}$ (“up” spin) or $-\frac{1}{2}$ (“down” spin)

• We represent the two spin states of the electron by two spin wavefunctions $\alpha(\omega)$ and $\beta(\omega)$ which are orthonormal:

$$\int \alpha^*(\omega)\alpha(\omega)\,d\omega = \int \beta^*(\omega)\beta(\omega)\,d\omega = 1$$

$$\int \alpha^*(\omega)\beta(\omega)\,d\omega = \int \beta^*(\omega)\alpha(\omega)\,d\omega = 0$$
Spatial and spin coordinates

• To describe the spin of an electron we include an extra “spin-coordinate”

• Therefore, for electron we have not only its three spatial coordinates \( x, y, z (=r) \) but also by its spin coordinate \( \omega \)

• We will denote these four coordinates collectively by \( x \)

\[
x = \{ r, \omega \}
\]

• Particles whose spin quantum number \( s \) is a half-integer (e.g. 1/2, 3/2, 5/2, etc.) are called Fermions.

• Electrons and protons are examples of Fermions

• Particles whose spin quantum number \( s \) is an integer (e.g. 1, 2, 3) are called Bosons. Photons are examples of Bosons
Antisymmetry of electronic wavefunctions

• Wavefunctions of Fermions change sign when the coordinates (space and spin) of any two particles are exchanged.

• This property is called antisymmetry:

\[ \Psi(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N) = -\Psi(x_1, \ldots, x_j, \ldots, x_i, \ldots, x_N) \]

• Electrons are Fermions, therefore electronic wavefunctions must be antisymmetric

• We need to include antisymmetry in all approximate wavefunctions we construct
Spin needs to be taken into account in all expressions

Examples (with normalised wavefunctions):

Electronic density

\[ n(r) = N_{el} \int \cdots \int \Psi^*(r, \omega_1, r_2, \omega_2, \cdots, r_{N_{el}}, \omega_{N_{el}}) \Psi(r, \omega_1, r_2, \omega_2, \cdots, r_{N_{el}}, \omega_{N_{el}}) \, d\omega_1 \, dr_2 \omega_2 \cdots \, dr_{N_{el}} \, d\omega_{N_{el}} \]

Electronic kinetic energy

\[ E_{kin} = \int \cdots \int \Psi^*(r_1, \omega_1, r_2, \omega_2, \cdots, r_{N_{el}}, \omega_{N_{el}}) \sum_{n=1}^{N_{el}} -\frac{1}{2} \nabla^2_n \Psi(r_1, \omega_1, r_2, \omega_2, \cdots, r_{N_{el}}, \omega_{N_{el}}) \, dr_1 \, d\omega_1 \, dr_2 \omega_2 \cdots \, dr_{N_{el}} \, d\omega_{N_{el}} \]
Electronic density vs electronic wavefunction

• The quantum theory is developed in terms of the wavefunction, which is a function of $4xN_{el}$ variables

$$\Psi \left( r_1, \omega_1, r_2, \omega_2, \ldots, r_{N_{el}}, \omega_{N_{el}} \right) = \Psi \left( x_1, x_2, \ldots, x_{N_{el}} \right)$$

• The electronic density is much simpler: It is a function of only 3 variables and has direct experimental relevance (e.g. Can be observed by X-ray diffraction)

$$n(r) = N_{el} \int \cdots \int \Psi^*(r, \omega_1, r_2, \omega_2, \ldots, r_{N_{el}}, \omega_{N_{el}}) \Psi(r, \omega_1, r_2, \omega_2, \ldots, r_{N_{el}}, \omega_{N_{el}}) \; d\omega_1 \; dr_2 \omega_2 \cdots dr_{N_{el}} \omega_{N_{el}}$$

(Worked example: lets examine how this expression is derived)

• However the Schrödinger equation involves the wavefunction, not the density
Example: Electronic density of a dipeptide (Ala-Gly)

Isovalue surfaces

\[ n(\mathbf{r}) = 3.0 \text{ e/a}_0^3 \]

\[ n(\mathbf{r}) = 1.5 \text{ e/a}_0^3 \]

\[ n(\mathbf{r}) = 0.75 \text{ e/a}_0^3 \]

\[ n(\mathbf{r}) = 0.3 \text{ e/a}_0^3 \]
What can we learn from the density

Example: Density of HeH$^+$

- The positions of the nuclei (cusps of the density)
- Their atomic numbers (from the slope of the density near the nuclei)
- The total number of electrons

\[ N_{el} = \int n(r) \, dr \]
In principle, you can obtain the energy from the density, but only indirectly.

Obtain number of electrons, atomic numbers, atomic positions

Calculate energy and other experimental observables from wavefunction

Is there a way to go from the density directly to the energy without having to solve the Schrödinger equation?
1) For the He atom the wavefunction is approximated in terms of 1s atomic orbitals, one occupied by an up spin electron and one occupied by a down spin electron. Which of the following possible wavefunctions is antisymmetric (note that we are using a shorthand notation where “1” means the spin and space coordinates of electron 1, etc):

\[ \Psi(1, 2) = \psi_{1s}^\alpha(1) \psi_{1s}^\beta(2) \]
\[ \Psi(1, 2) = \psi_{1s}^\alpha(1) \psi_{1s}^\beta(2) + \psi_{1s}^\alpha(2) \psi_{1s}^\beta(1) \]
\[ \Psi(1, 2) = \psi_{1s}^\alpha(1) \psi_{1s}^\beta(2) - \psi_{1s}^\alpha(2) \psi_{1s}^\beta(1) \]

2) The term “external potential” is often used to refer to the potential energy operator for attraction of the electrons to the nuclei. For example, the external potential of a HeH ion is

\[ V_{\text{ext}}(r) = -\frac{1}{|r - R_H|} - \frac{2}{|r - R_{\text{He}}|} \]

Write down an expression for the external potential of the Hamiltonian operator for the water molecule from slide 5.

3) Taking into account the indistinguishability of electrons, show how the external potential energy (see previous question)

\[ \int \cdots \int \psi^* \left( \sum_{i=1}^{N_e} V_{\text{ext}}(r_i) \right) \psi \, dx_1 \cdots dx_{N_e} \]

Can be equivalently written as

\[ \int V_{\text{ext}}(r) \, n(r) \, dr \]

Which is an expression involving the density instead of the wavefunction.
5-minute quiz

Name: 
Surname: 

Date: 

1) Which of the following types of information do we need in order to write down the electronic Hamiltonian operator for a molecule?
   a) The position of each nucleus
   b) The atomic number of each nucleus
   c) The mass of each nucleus
   d) The spin of each nucleus
   e) The total number of electrons

2) Which of the above can be obtained by examination of the electronic density and how?

3) For the He atom the wavefunction is approximated as a product of 1s atomic orbitals, one occupied by an up spin electron and one occupied by a down spin electron as \( \Psi(x_1, x_2) = \psi^\alpha_1(x_1) \psi^\beta_1(x_2) \). Find an expression for the electronic density given that the atomic orbitals obtain the following condition (normalisation):

\[
\int |\psi^\alpha_1(x)|^2 \, dx = \int |\psi^\beta_1(x)|^2 \, dx = 1
\]