

CHEM6085: Density Functional Theory

Lecture 3

Electronic wavefunctions and electronic density

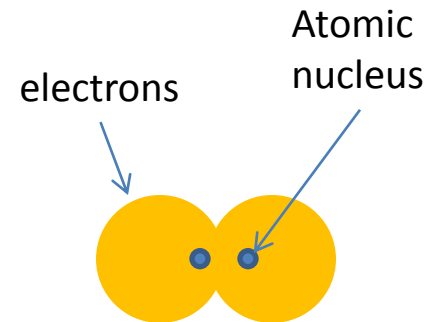
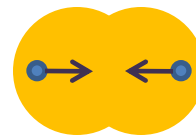
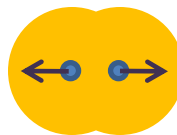
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The Born-Oppenheimer approximation

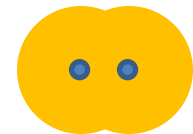
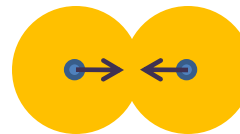
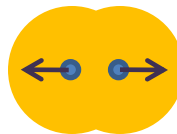
- Nuclei are much heavier than electrons and move at much slower speeds
- For example, the nuclei in H_2 move only about 1pm for each 1000pm of electronic motion
- To a very good approximation, we can assume that the electronic motions are instantaneously “equilibrated” at each nuclear position

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:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}}, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_{\text{atoms}}})$$

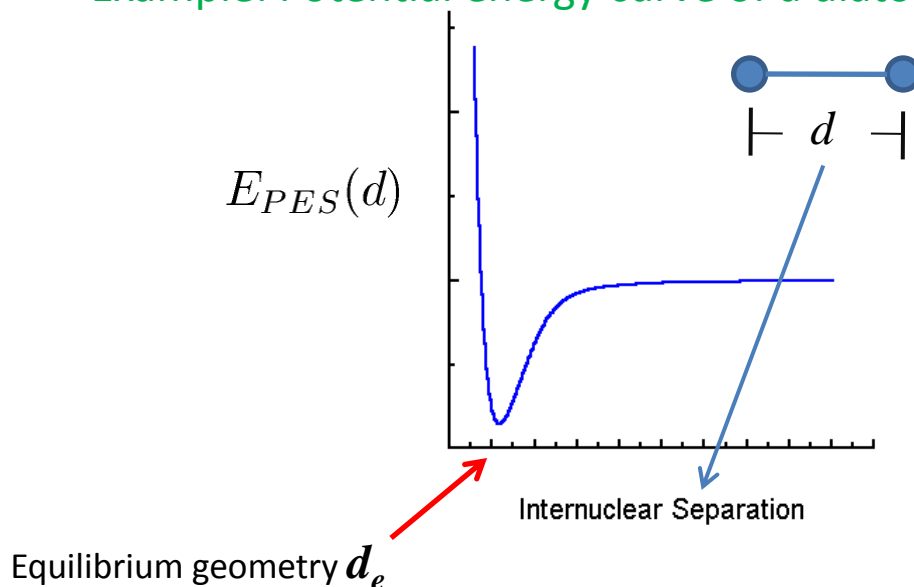
- The Born-Oppenheimer approximation is based on the fact that nuclei have much larger masses than the electrons
- To a good approximation, one can solve the Schrödinger equation only for the electrons and assume the nuclei are frozen
- We will use this approximation from now on
- As a result, our wavefunctions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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{electrons}}})$$

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



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.

$$\hat{H}_{H_2O} = -\frac{\cancel{1}^{\text{B.O.}}}{\cancel{2M_O}} \nabla_{\mathbf{R}_O}^2 - \frac{\cancel{1}^{\text{B.O.}}}{\cancel{2M_{H1}}} \nabla_{\mathbf{R}_{H1}}^2 - \frac{\cancel{1}^{\text{B.O.}}}{\cancel{2M_{H2}}} \nabla_{\mathbf{R}_{H2}}^2 - \sum_{i=1}^{10} \frac{1}{2} \nabla_{\mathbf{r}_i}^2$$

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

$$- \sum_{i=1}^{10} \frac{8}{|\mathbf{r}_i - \mathbf{R}_O|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H1}|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H2}|}$$

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

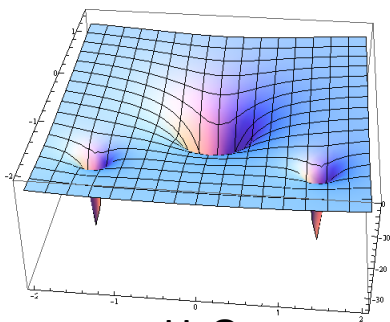
$$+ \sum_{i=1}^{10} \sum_{j=i+1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I=1}^3 \sum_{J=I+1}^3 \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electron-electron repulsion
 nucleus-nucleus repulsion

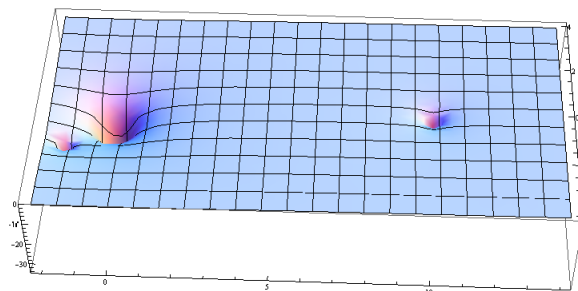
E.g. Assume
 $Z_1=Z_O$
 $Z_2=Z_{H1}$
 $Z_3=Z_{H2}$

- 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

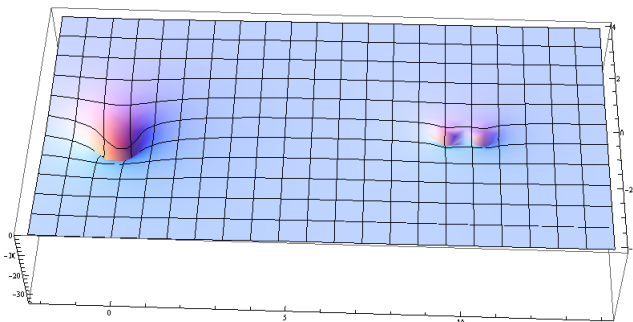
Example: Nuclear attraction potential for one O and two H



H₂O



OH + H



O + H₂

- How does the Hamiltonian operator differ between these examples?
- Can you suggest how you may model the reaction $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$

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 $s=1/2$, and its z-component $m_s = 1/2$ (“up” spin) or $-1/2$ (“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

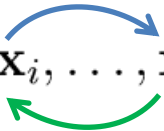
- To describe the spin of an electron we include an extra “spin-coordinate”
- Therefore, for electron we have not only its three spatial coordinates x, y, z ($=\mathbf{r}$) but also by its spin coordinate ω
- We will denote these four coordinates collectively by \mathbf{x}

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

- 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:

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


- 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

$$n(\mathbf{r}) = N_{el} \int \cdots \int \Psi^*(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \cdots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) \Psi(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \cdots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) d\omega_1 d\mathbf{r}_2 d\omega_2 \cdots d\mathbf{r}_{N_{el}} d\omega_{N_{el}}$$

Electronic kinetic energy

$$E_{kin} = \int \cdots \int \Psi^*(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2, \cdots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) \sum_{n=1}^{N_{el}} -\frac{1}{2} \nabla_n^2 \Psi(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2, \cdots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \cdots d\mathbf{r}_{N_{el}} d\omega_{N_{el}}$$

Electronic density vs electronic wavefunction

- The quantum theory is developed in terms of the wavefunction, which is a function of $4 \times N_{el}$ variables

$$\Psi(\mathbf{r}_1, \omega_1, \mathbf{r}_2, \omega_2, \dots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{N_{el}})$$

- 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)

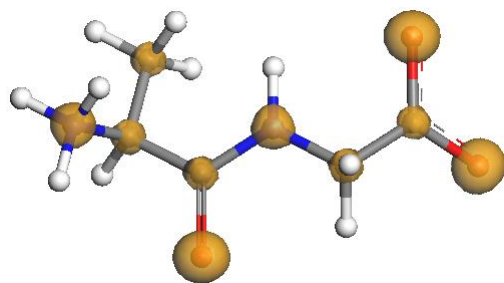
$$n(\mathbf{r}) = N_{el} \int \dots \int \Psi^*(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \dots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) \Psi(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \dots, \mathbf{r}_{N_{el}}, \omega_{N_{el}}) d\omega_1 d\mathbf{r}_2 d\omega_2 \dots d\mathbf{r}_{N_{el}} d\omega_{N_{el}}$$

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

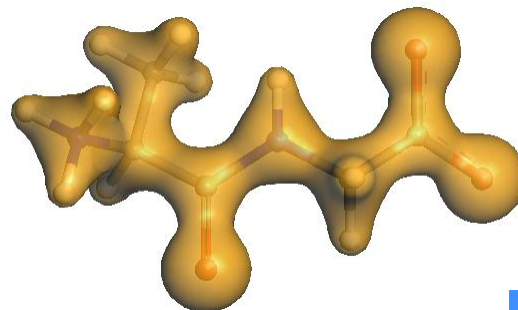
- However the Schrödinger equation involves the wavefunction, not the density

Example: Electronic density of a dipeptide (Ala-Gly)

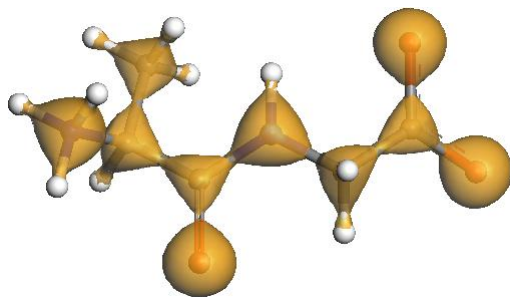
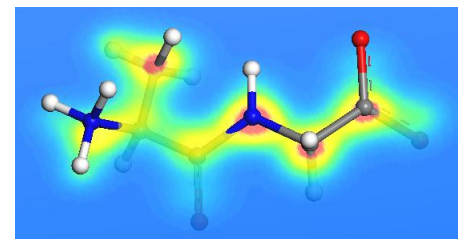
Isovalue surfaces



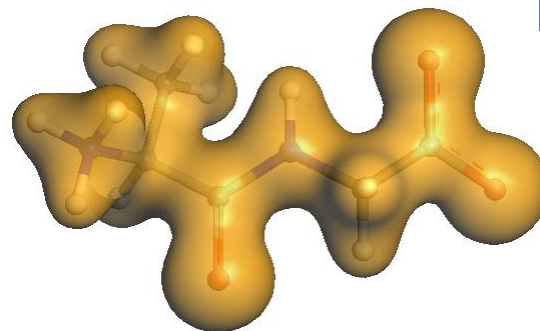
$$n(\mathbf{r})=3.0 \text{ e}/a_0^3$$



$$n(\mathbf{r})=0.75 \text{ e}/a_0^3$$



$$n(\mathbf{r})=1.5 \text{ e}/a_0^3$$



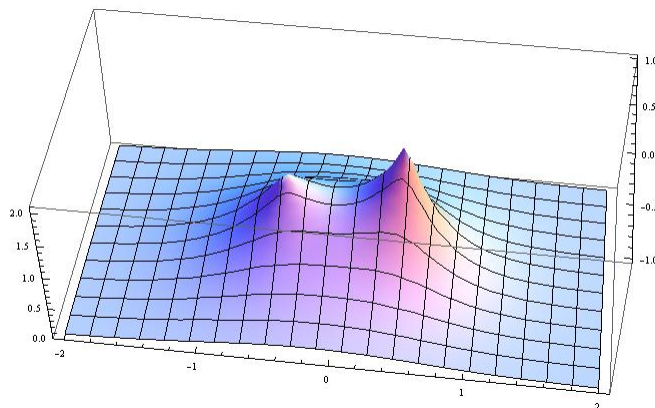
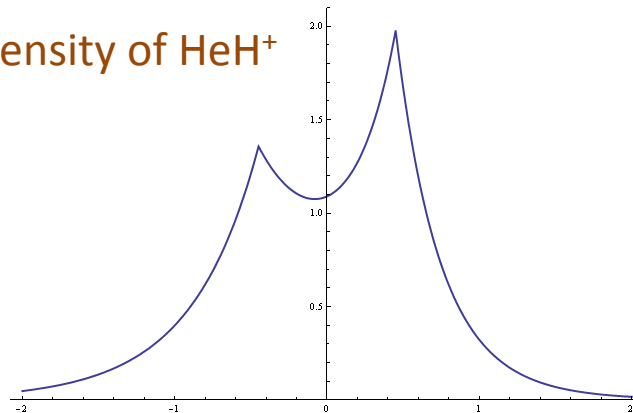
$$n(\mathbf{r})=0.3 \text{ e}/a_0^3$$

What can we learn from the density

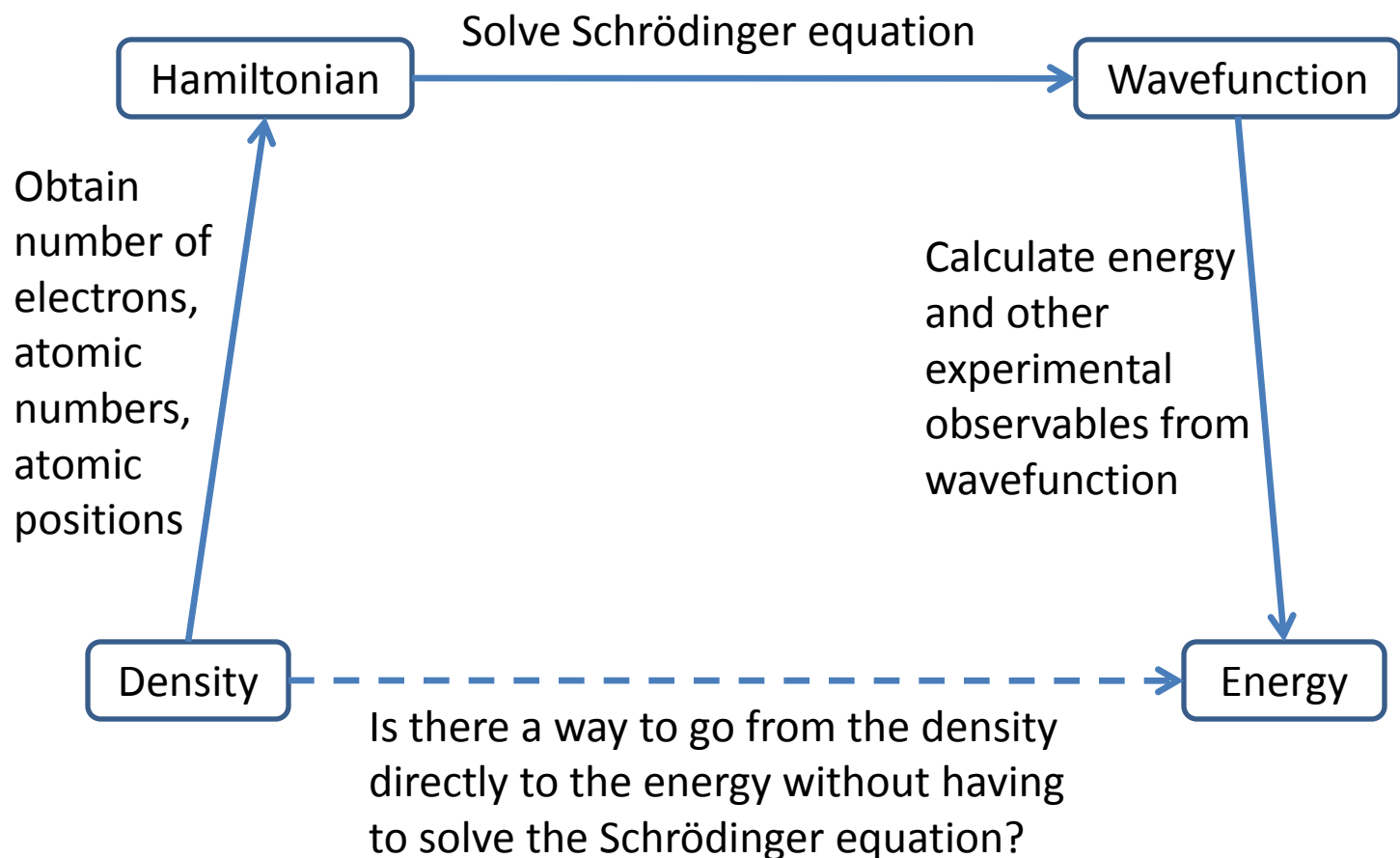
- The positions of the nuclei (cusps of the density)
- Their atomic numbers (from the slope of the density near the nuclei)
- The total number of electrons

$$N_{el} = \int n(\mathbf{r}) d\mathbf{r}$$

Example: Density of HeH⁺



In principle, you can obtain the energy from the density, but only indirectly



Homework

- 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 if 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 $V_{\text{ext}}(\mathbf{r}) = -\frac{1}{|\mathbf{r} - \mathbf{R}_{\text{H}}|} - \frac{2}{|\mathbf{r} - \mathbf{R}_{\text{He}}|}$. 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)

$$\int \cdots \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}(\mathbf{r}_i) \right) \Psi d\mathbf{x}_1 \cdots d\mathbf{x}_{N_{\text{el}}}$$

can be equivalently written as $\int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$ 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 ?
- The position of each nucleus
 - The atomic number of each nucleus
 - The mass of each nucleus
 - The spin of each nucleus
 - 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 $\Psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_{1s}^\alpha(\mathbf{x}_1) \psi_{1s}^\beta(\mathbf{x}_2)$. Find an expression for the electronic density given that the atomic orbitals obtain the following condition (normalisation):

$$\int |\psi_{1s}^\alpha(\mathbf{x})|^2 d\mathbf{x} = \int |\psi_{1s}^\beta(\mathbf{x})|^2 d\mathbf{x} = 1$$