

- Helium atom,  $Z = 2$ , to illustrate.

Kinetic energy of 1st electron, its attraction to doubly charged nucleus, kinetic energy of 2nd electron, its attraction to nucleus, repulsion between the two electrons.

$$\hat{H} = \hat{H}_0 + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|} \text{ where}$$

$$\hat{H}_0 = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0r_2}\right).$$

- $\hat{H}\Psi_\lambda = E_\lambda\Psi_\lambda$ .
- $\Psi_\lambda(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = -\Psi_\lambda(\mathbf{r}_2, \sigma_2, \mathbf{r}_1, \sigma_1)$ .

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- Ignoring the e-e interactions  $\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3$  where  $\hat{H}_1$  is Hamiltonian for electron 1 moving in a potential set by a  $Z = 3$  nucleus with  $E_n = -3^2 \frac{13.6}{n^2}$  etc.
- Ground state energy  $E_g$  for the three electrons is  $(E_1 + E_1 + E_2)$ , i.e. one electron with spin  $\uparrow$  occupies an energy  $E_1$ , one with spin  $\downarrow$  also with  $E_1$  and one with  $E_2$  ( $1s^2 2s^1$ ).  $E_g = -3^2\left(\frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2}\right) 13.6$  eV, i.e. -275.4 eV.

# Model of a single electron in an 'effective potential'

- Back to the helium atom: an approximation for the ground state wavefunction  $\Psi = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) (\uparrow\downarrow)$
- The 'best'  $\phi(\mathbf{r})$  function found from solving this equation for a single electron moving in a potential  $V_s(\mathbf{r}) = -\frac{2e^2}{4\pi\epsilon_0 r} + e \int \int \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r}-\mathbf{r}'|} dV'$  and the charge density  $\rho(\mathbf{r})$  comes from  $e\phi(\mathbf{r})^*\phi(\mathbf{r})$  (from the other electron).
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- Picture of single electron moving in a potential set up by nucleus and charge from the other electron. - *Hartree (Hartree-Fock) approximation.*
- Example of a more general picture: Many electrons modelled as independent electrons moving in a potential set up by the (fixed) nuclei and all the other electrons.
- The Hartree approximation for this:  
$$V_s(\mathbf{r}) = -\sum_I \frac{Z_I e^2}{4\pi\epsilon_0 |\mathbf{r}-\mathbf{R}_I|} + e \int \int \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r}-\mathbf{r}'|} dV',$$
$$\rho(\mathbf{r}) = e \sum_{\lambda=\lambda_1}^{\lambda_n} \phi(\mathbf{r})_{\lambda}^* \phi(\mathbf{r})_{\lambda}.$$
  $\lambda$  sum runs over set of single electron states filled up using all the other  $n - 1$  electrons.

# Computational method for studying electrons in matter

- Computational materials modelling must describe order of magnitude  $10^{24}$  interacting electrons.
- Density functional theory (DFT) makes this problem tractable. It focuses on dependence of the energy of a material on electronic charge  $\rho$  (and magnetisation) density.
- Many interacting electrons described in terms of non-interacting electrons in effective fields.

Walter Kohn, Nobel Prize 1998  
Chemistry



Walter Kohn



Papers including DFT calculations

