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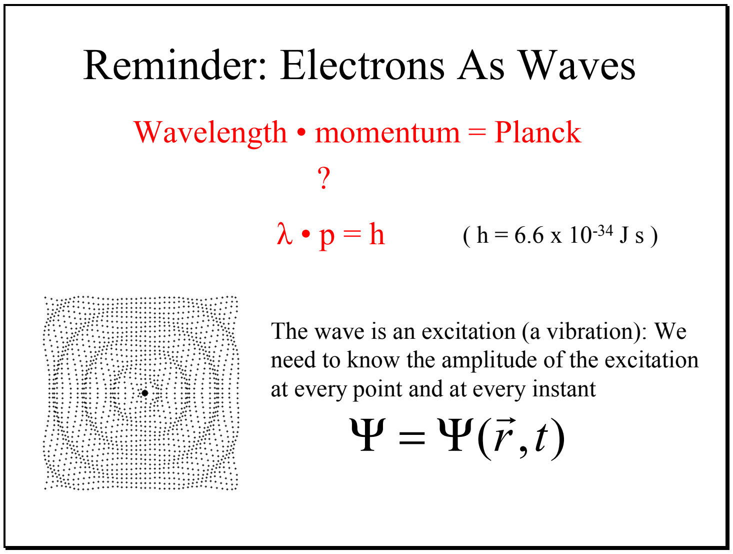
Quantum Mechanics: the Practice



Reminder: Electrons As Waves

Wavelength • momentum = Planck

?

$\lambda \cdot p = h$ ($h = 6.6 \times 10^{-34}$ J s)

The wave is an excitation (a vibration): We need to know the amplitude of the excitation at every point and at every instant

$$\Psi = \Psi(\vec{r}, t)$$

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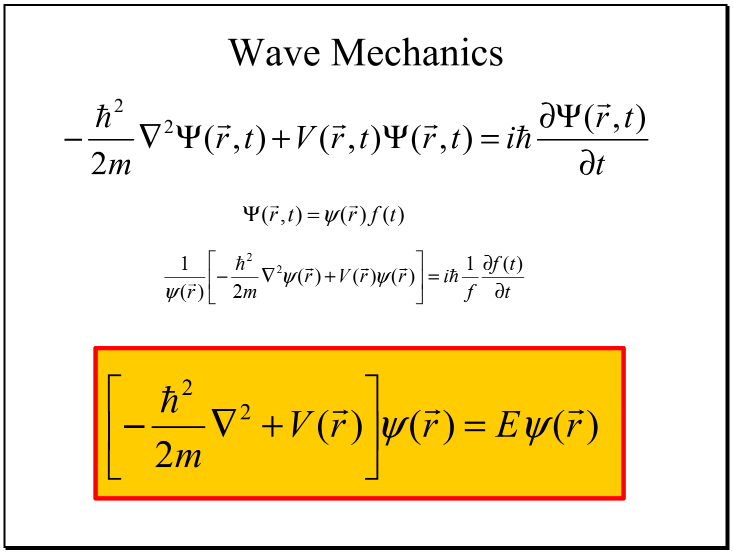


Wave Mechanics

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V(\vec{r},t)\Psi(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

$$\Psi(\vec{r},t)=\psi(\vec{r})f(t)$$

$$\frac{1}{\psi(\vec{r})}\left[-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V(\vec{r})\psi(\vec{r})\right]=i\hbar\frac{1}{f}\frac{\partial f(t)}{\partial t}$$

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\psi(\vec{r})=E\psi(\vec{r})}$$

Stationary Schroedinger's equation

$$(a) \qquad \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}$$

$$(b) \qquad \hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

- It's not proven – it's postulated, and it is confirmed experimentally
- It's an eigenvalue equation
- Boundary conditions (and regularity) must be specified

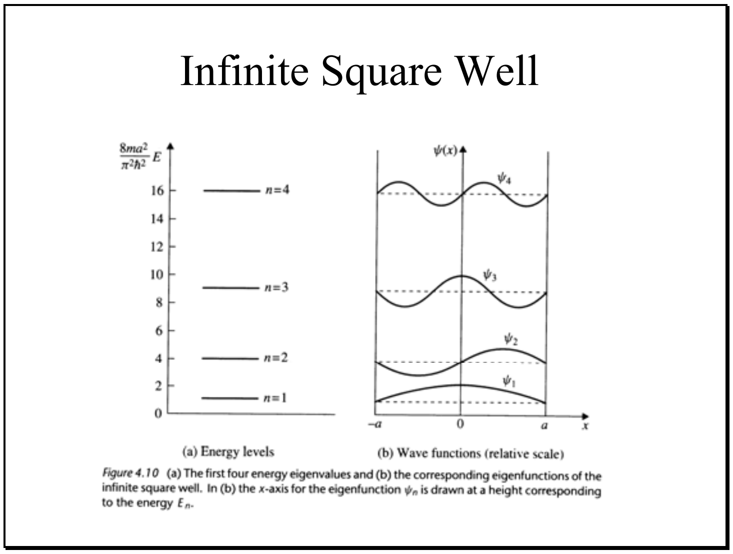
Interpretation of the Quantum Wavefunction

$\left\|\Psi(\vec{r},t)\right\|^2$ is the probability of finding an electron in *r* and *t*

If V=V(r) , it's separable: $\Psi(\vec{r},t)=\psi(\vec{r})f(t)=\psi(\vec{r})\exp(-\frac{i}{\hbar}Et)$

Remember the free particle, and the principle of indetermination:if the momentum is perfectly known, the position is perfectly unknown

$$\Psi(\vec{r},t)=A\exp[i(\vec{k}\bullet\vec{r}-\omega t)]$$



Infinite Square Well

(a) Energy levels

(b) Wave functions (relative scale)

Figure 4.10 (a) The first four energy eigenvalues and (b) the corresponding eigenfunctions of the infinite square well. In (b) the x-axis for the eigenfunction ψ_n is drawn at a height corresponding to the energy E_n.

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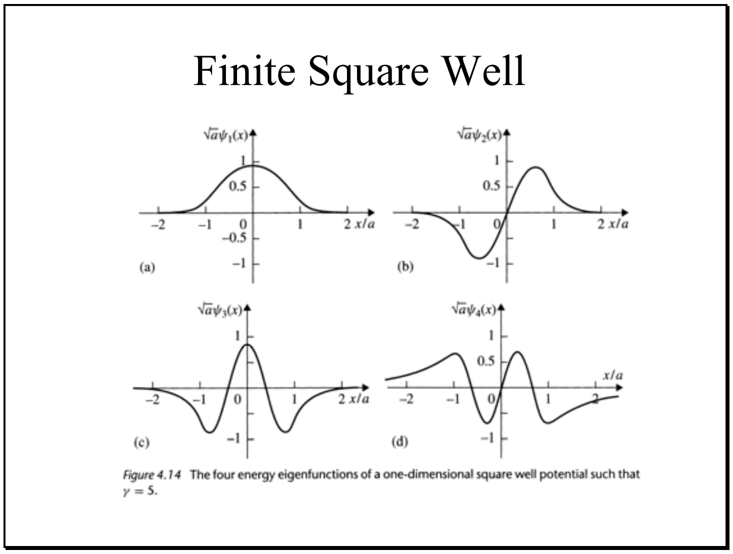

Finite Square Well

Figure 4.14 The four energy eigenfunctions of a one-dimensional square well potential such that $\gamma = 5$.

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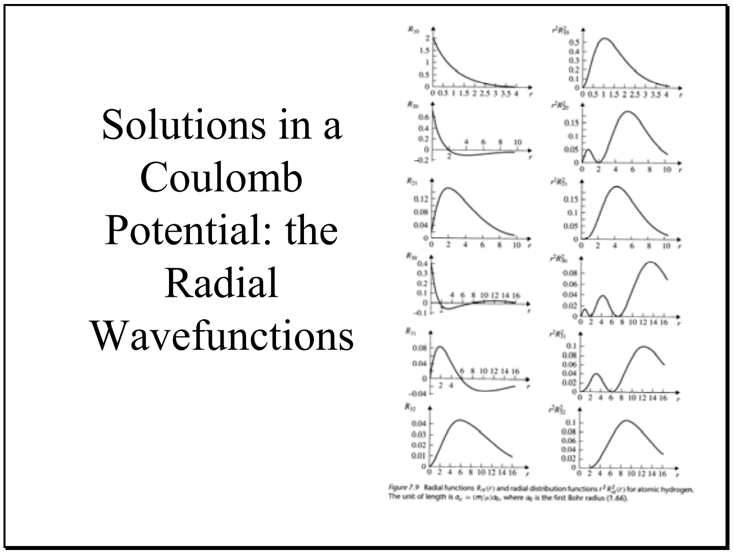
A Central Potential (e.g. the Nucleus)

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(\vec{r}) \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right] + V(r)$$

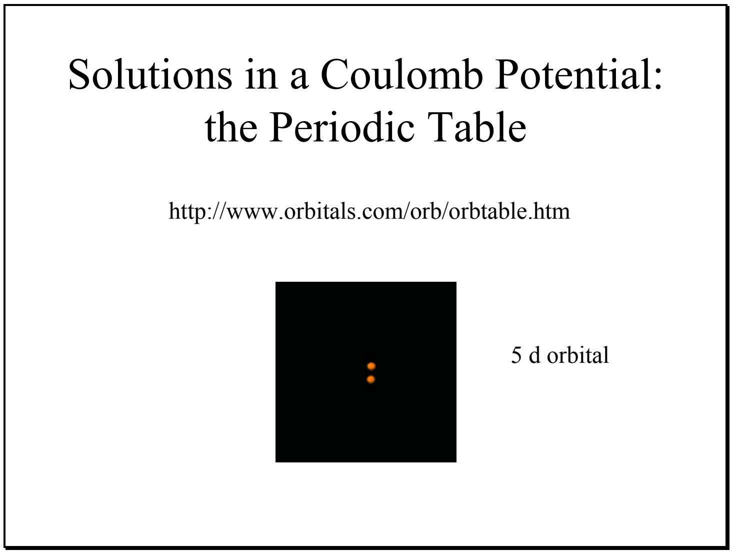
$$\psi_{Elm}(\vec{r}) = R_{Elm}(r)Y_{lm}(\vartheta,\varphi)$$

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right]R_{El}(r) = E\,R_{El}(r)$$



Solutions in a Coulomb Potential: the Radial Wavefunctions

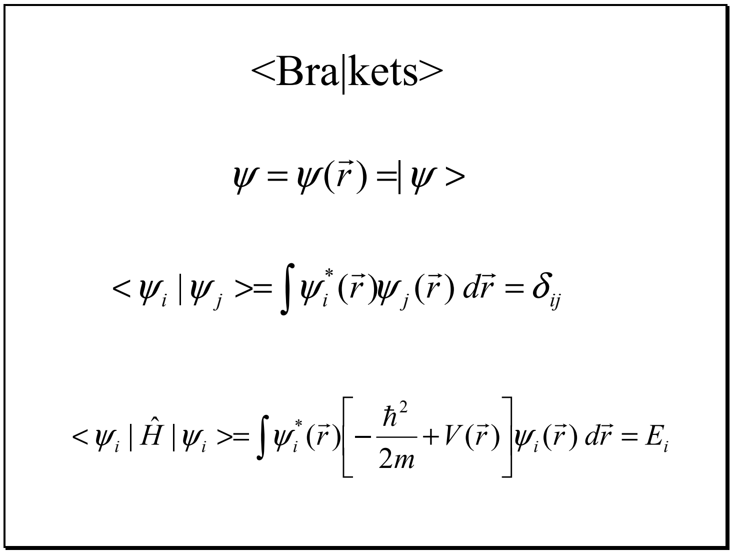
Figure 7.9 Radial functions $R_{n\ell}(r)$ and radial distribution functions $r^2R_{n\ell}^2(r)$ for atomic hydrogen. The unit of length is $a_\mu = (m/\mu)a_0$, where a_0 is the first Bohr radius (1.66).



Solutions in a Coulomb Potential: the Periodic Table

http://www.orbitals.com/orb/orbtable.htm

5 d orbital



<Bra|kets>

$$\psi = \psi(\vec{r}) = |\,\psi >$$

$$< \psi_i \,|\, \psi_j >= \int \psi_i^*(\vec{r}) \psi_j(\vec{r})\, d\vec{r} = \delta_{ij}$$

$$< \psi_i \,|\, \hat{H} \,|\, \psi_i >= \int \psi_i^*(\vec{r}) \left[-\frac{\hbar^2}{2m} + V(\vec{r}) \right] \psi_i(\vec{r})\, d\vec{r} = E_i$$

Variational Principle

$$E[\phi] = \frac{<\phi \mid \hat{H} \mid \phi>}{<\phi \mid \phi>}$$

$$E[\phi] \geq E_0$$

Electrons and Nuclei

$$\hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{N-N} + \hat{V}_{e-N}$$

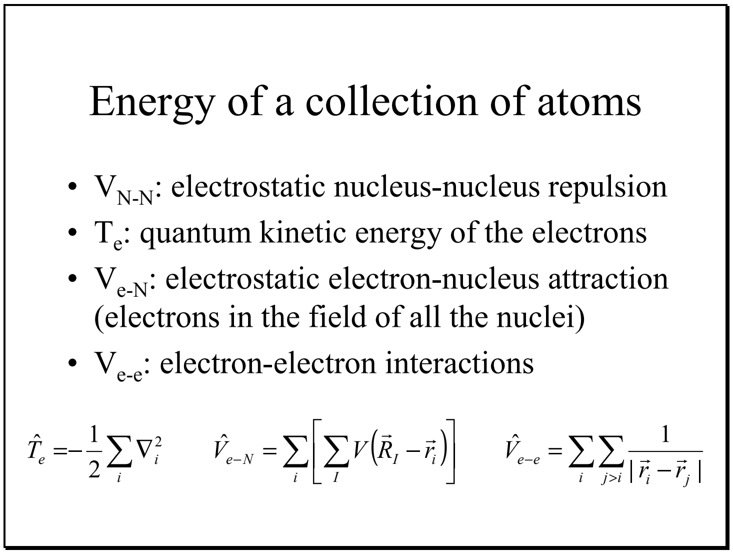
$$\hat{H}\psi(\vec{r}_1,\ldots,\vec{r}_n) = E_{tot}\psi(\vec{r}_1,\ldots,\vec{r}_n)$$

•We treat only the electrons as quantum particles, in the field of the fixed (or slowly varying) nuclei

•This is generically called the adiabatic or Born-Oppenheimer approximation

Two-electron atom

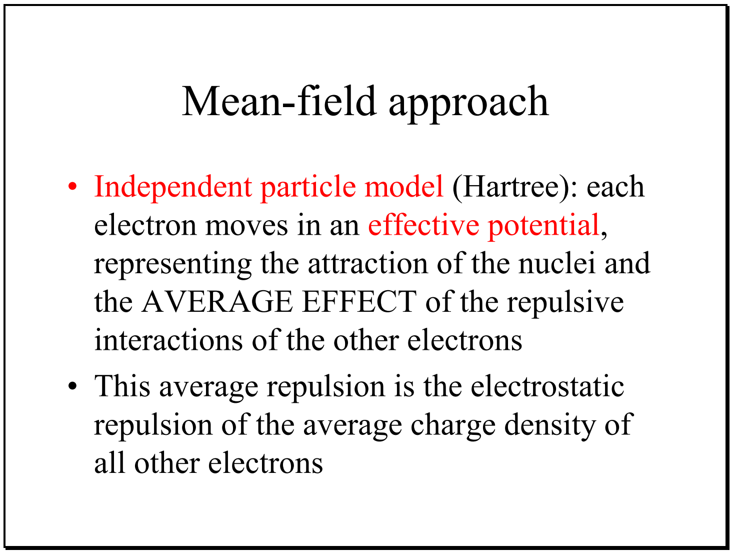
$$\left[-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{|\vec{r}_1-\vec{r}_2|}\right]\psi(\vec{r}_1,\vec{r}_2)=E\psi(\vec{r}_1,\vec{r}_2)$$



Energy of a collection of atoms

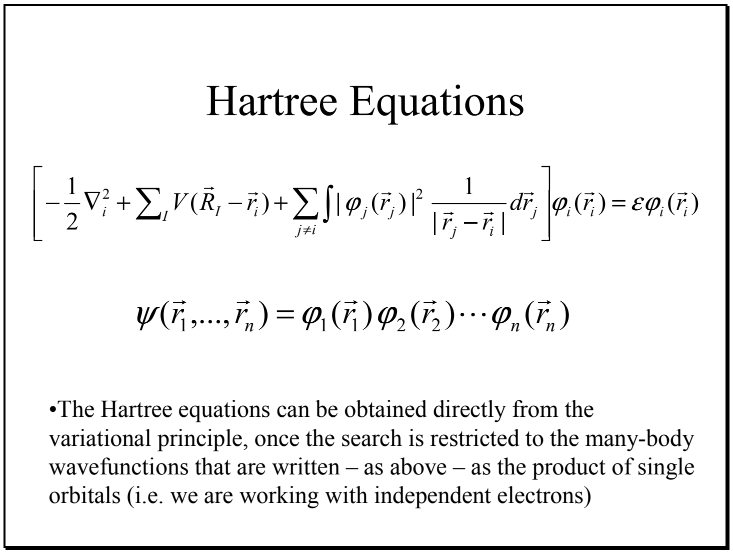
- $V_{N\text{-}N}$: electrostatic nucleus-nucleus repulsion
- T_e: quantum kinetic energy of the electrons
- $V_{e\text{-}N}$: electrostatic electron-nucleus attraction (electrons in the field of all the nuclei)
- $V_{e\text{-}e}$: electron-electron interactions

$$\hat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2 \qquad \hat{V}_{e-N} = \sum_i \left[\sum_I V\left(\vec{R}_I - \vec{r}_i\right) \right] \qquad \hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$



Mean-field approach

- Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the AVERAGE EFFECT of the repulsive interactions of the other electrons
- This average repulsion is the electrostatic repulsion of the average charge density of all other electrons

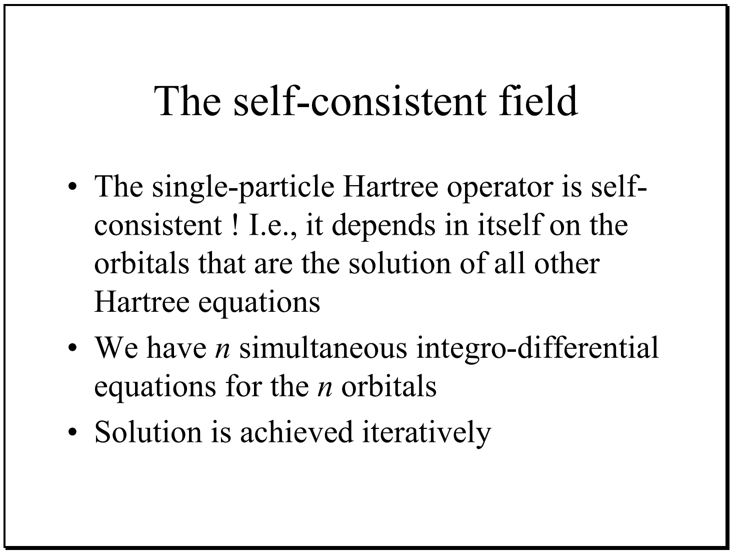


Hartree Equations

$$\left[-\frac{1}{2}\nabla_i^2+\sum\nolimits_I V(\vec{R}_I-\vec{r}_i)+\sum_{j\neq i}\int|\varphi_j(\vec{r}_j)|^2\frac{1}{|\vec{r}_j-\vec{r}_i|}d\vec{r}_j\right]\varphi_i(\vec{r}_i)=\varepsilon\varphi_i(\vec{r}_i)$$

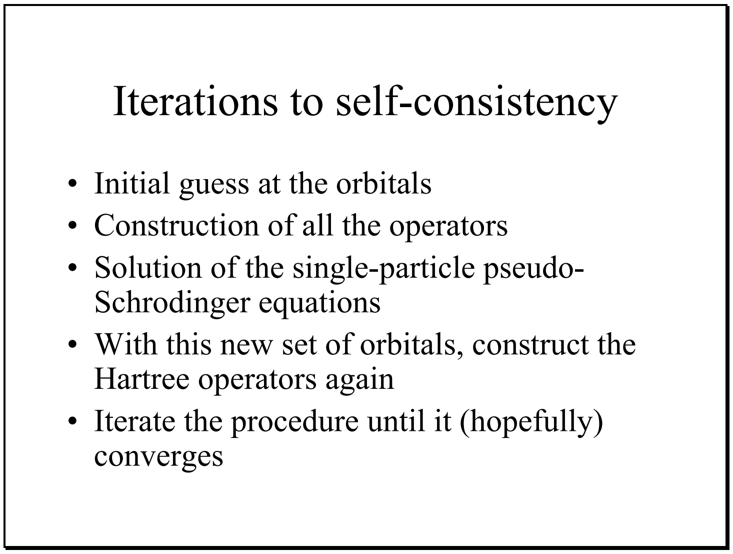
$$\psi(\vec{r}_1,\ldots,\vec{r}_n)=\varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2)\cdots\varphi_n(\vec{r}_n)$$

- The Hartree equations can be obtained directly from the variational principle, once the search is restricted to the many-body wavefunctions that are written – as above – as the product of single orbitals (i.e. we are working with independent electrons)



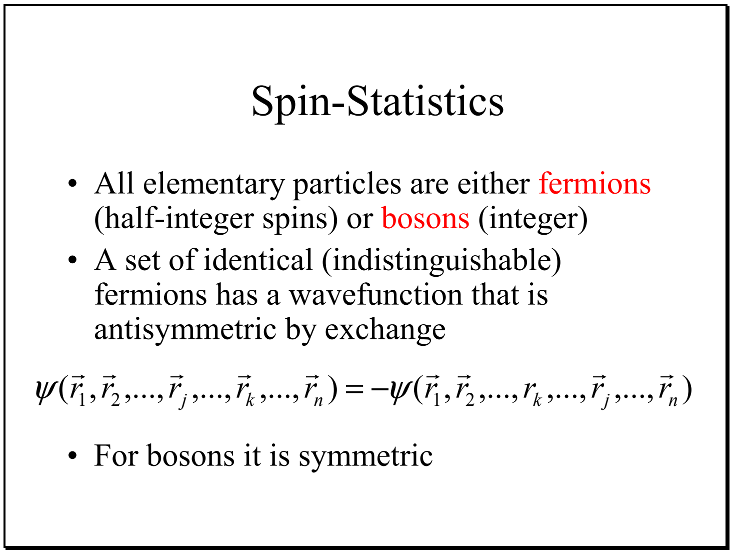
The self-consistent field

- The single-particle Hartree operator is self-consistent ! I.e., it depends in itself on the orbitals that are the solution of all other Hartree equations
- We have *n* simultaneous integro-differential equations for the *n* orbitals
- Solution is achieved iteratively



Iterations to self-consistency

- Initial guess at the orbitals
- Construction of all the operators
- Solution of the single-particle pseudo-Schrodinger equations
- With this new set of orbitals, construct the Hartree operators again
- Iterate the procedure until it (hopefully) converges



Spin-Statistics

- All elementary particles are either fermions (half-integer spins) or bosons (integer)
- A set of identical (indistinguishable) fermions has a wavefunction that is antisymmetric by exchange

$$\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_j,\ldots,\vec{r}_k,\ldots,\vec{r}_n) = -\psi(\vec{r}_1,\vec{r}_2,\ldots,r_k,\ldots,\vec{r}_j,\ldots,\vec{r}_n)$$

- For bosons it is symmetric

Slater determinant

- An antisymmetric wavefunction is constructed via a Slater determinant of the individual orbitals (instead of just a product, as in the Hartree approach)

$$\psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n)=\frac{1}{\sqrt{n!}}\begin{Vmatrix}\varphi_\alpha(\vec{r}_1) & \varphi_\beta(\vec{r}_1) & \cdots & \varphi_\nu(\vec{r}_1)\\ \varphi_\alpha(\vec{r}_2) & \varphi_\beta(\vec{r}_2) & \cdots & \varphi_\nu(\vec{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \varphi_\alpha(\vec{r}_n) & \varphi_\beta(\vec{r}_n) & \cdots & \varphi_\nu(\vec{r}_n)\end{Vmatrix}$$

Pauli principle

- If two states are identical, the determinant vanishes (I.e. we can’t have two electrons in the same quantum state)

Hartree-Fock Equations

- The Hartree-Fock equations are, again, obtained from the variational principle: we look for the minimum of the many-electron Schroedinger equation in the class of all wavefunctions that are written as a single Slater determinant

$$\left[-\frac{1}{2}\nabla_i^2+\sum_I V(\vec{R}_I-\vec{r}_i)\right]\varphi_\lambda(\vec{r}_i)+$$

$$\left[\sum_\mu \int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j-\vec{r}_i|}\varphi_\mu(\vec{r}_j)\,d\vec{r}_j\right]\varphi_\lambda(\vec{r}_i)-$$

$$\sum_\mu\left[\int \varphi_\mu^*(\vec{r}_j)\frac{1}{|\vec{r}_j-\vec{r}_i|}\varphi_\lambda(\vec{r}_j)d\vec{r}_j\right]\varphi_\mu(\vec{r}_i)=\varepsilon\varphi_\lambda(\vec{r}_i)$$

$$\psi(\vec{r}_1,\ldots,\vec{r}_n)=\|Slater\|$$

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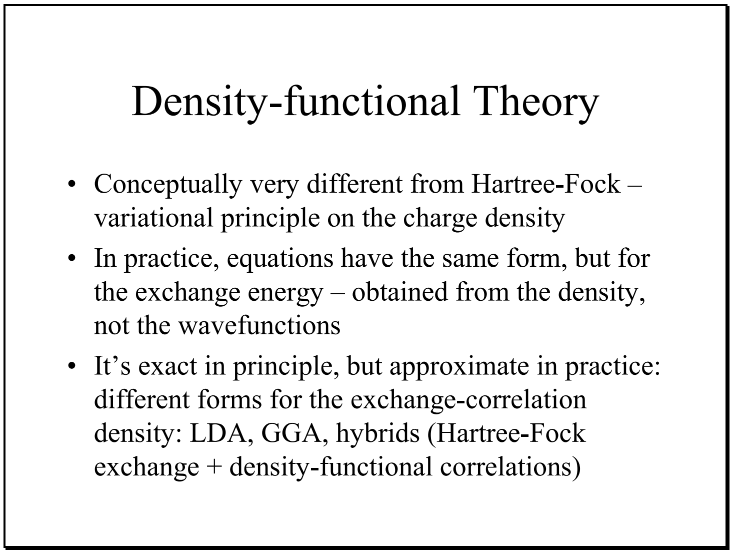

Density-functional Theory

- Conceptually very different from Hartree-Fock – variational principle on the charge density
- In practice, equations have the same form, but for the exchange energy – obtained from the density, not the wavefunctions
- It’s exact in principle, but approximate in practice: different forms for the exchange-correlation density: LDA, GGA, hybrids (Hartree-Fock exchange + density-functional correlations)