3.320: Lecture 5 (Feb 15 2005)

THE MANY-BODY PROBLEM

When is a particle like a wave ?

Wavelength • momentum = Planck

$$\updownarrow$$

$$\lambda \bullet p = h \qquad (\, h = 6.6 \text{ x } 10^{-34} \text{ J s} \,)$$
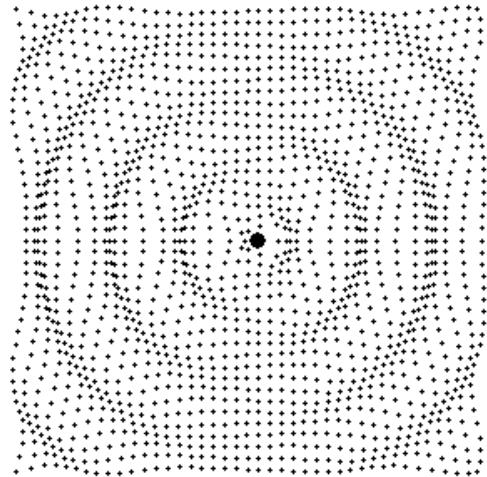
$$\Psi = \Psi(\vec{r}, t)$$

Time-dependent Schrödinger's equation
(Newton's 2nd law for quantum objects)

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

1925-onwards: E. Schrödinger (wave equation), W. Heisenberg (matrix formulation), P.A.M. Dirac (relativistic)

Stationary Schrödinger's Equation (I)

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

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

$$-\frac{\hbar^2}{2m}f\nabla^2\varphi + V\varphi f = i\hbar\varphi\frac{\partial f}{\partial t} \Bigg/ \varphi f$$

$$-\frac{\hbar^2}{2m}\frac{\nabla^2\varphi}{\varphi} + V = i\hbar\frac{1}{f}\frac{\partial f}{\partial t}$$

ONLY $\vec{r}$

DEPENDS ONLY ON t

Stationary Schrödinger's Equation (II)

$$i\hbar \frac{d}{dt} f(t) = E f(t)$$

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

$$i\hbar \frac{d}{dt} f(t) = E f(t)$$
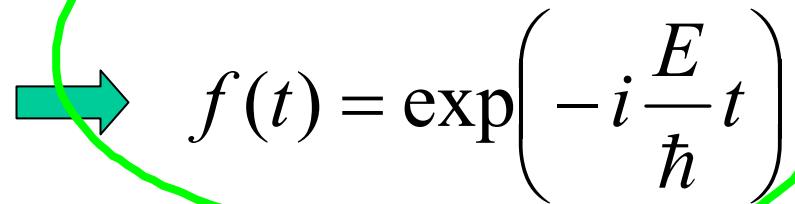
$$f(t) = \exp\left(-i\frac{E}{\hbar}t\right)$$

Free particle $\Psi(x,t) = \varphi(x)f(t)$

$$-\frac{\hbar^2}{2m}\nabla^2 \varphi(x) = E\varphi(x)$$
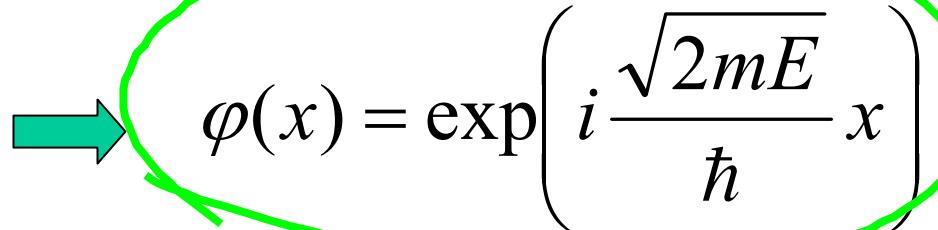
$$\varphi(x) = \exp\left(i\frac{\sqrt{2mE}}{\hbar}x\right)$$

$$\nabla^2 \varphi = -\frac{2mE}{\hbar^2}\varphi$$

Interpretation of the Quantum Wavefunction (Copenhagen)

$$\left\|\Psi(x,t)\right\|^2$$

is the probability of finding an electron in x and t

$$\|\Psi\|^2 = \Psi\Psi^*$$

$$\left\|\varphi(x)\exp\left(-\frac{i}{\hbar}Et\right)\right\|^2 = \left\|\varphi(x)\right\|^2$$

A Traveling "Plane" Wave

$$\Psi(x,t) \propto \exp[i(kx - \omega t)]$$

$\vec{k} \cdot \vec{r}$
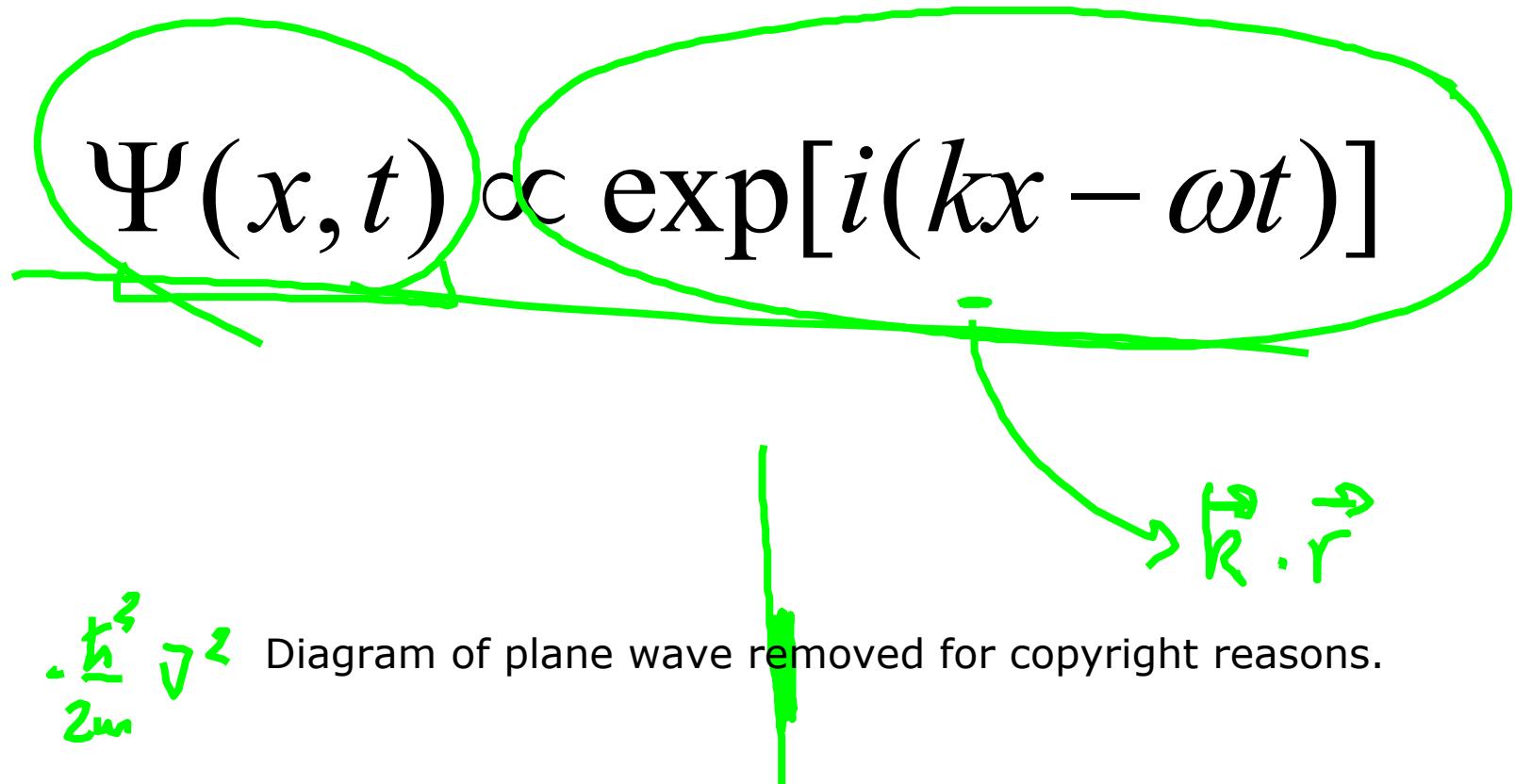
$\hat{T} = -\dfrac{\hbar^2}{2m}\nabla^2$

Diagram of plane wave removed for copyright reasons.

$n = n_1$

Feb 15 2005   3.320 Atomistic Modeling of Materials -- Gerbrand Ceder and Nicola Marzari

Metal Surfaces (I)

$$V(x), V_0, 0, x$$
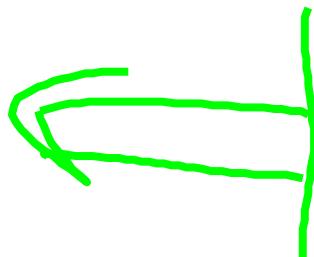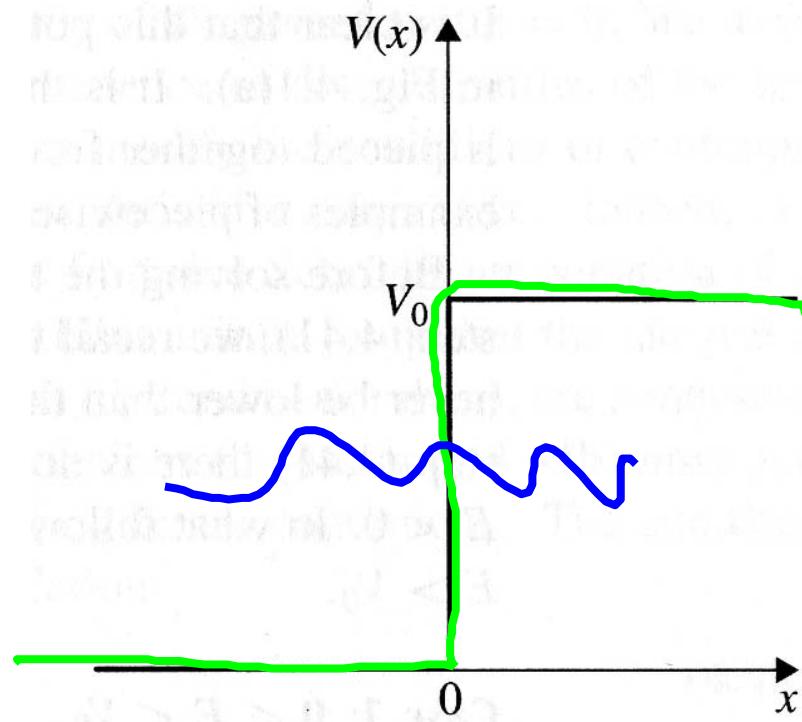
$$\text{DFT} \rightarrow -\frac{\hbar^2}{2m}\nabla^2\varphi = E\varphi$$

$$\text{96HT} \rightarrow -\frac{\hbar^2}{2m}\nabla^2\varphi + V_0\varphi = E\varphi$$

$$-\frac{\hbar^2}{2m}\nabla^2\varphi = (E-V_0)\varphi$$

Metal Surfaces (II)
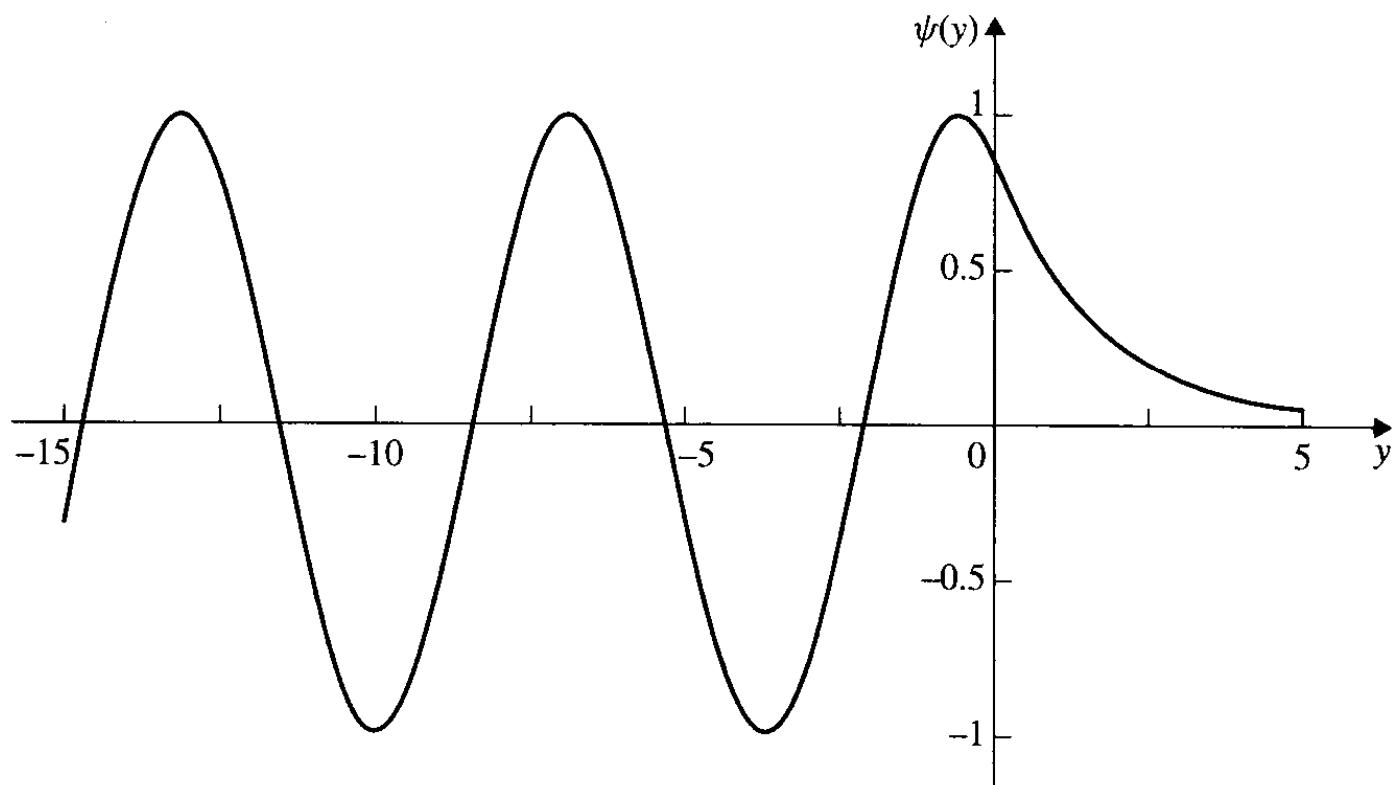
Infinite Square Well
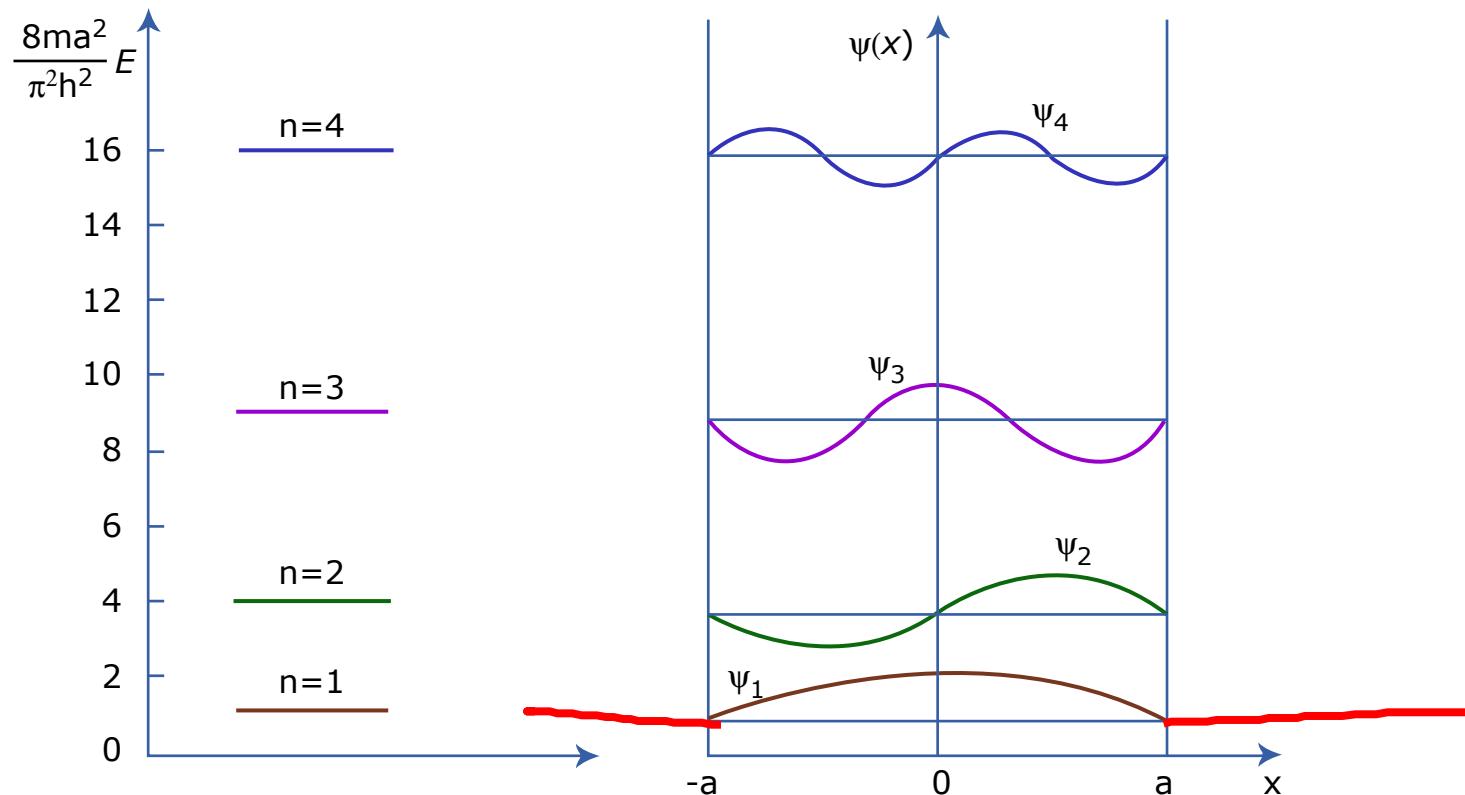
Figure by MIT OCW.

Finite Square Well

Figure by MIT OCW.

Feb 15 2005   3.320 Atomistic Modeling of Materials -- Gerbrand Ceder and Nicola Marzari
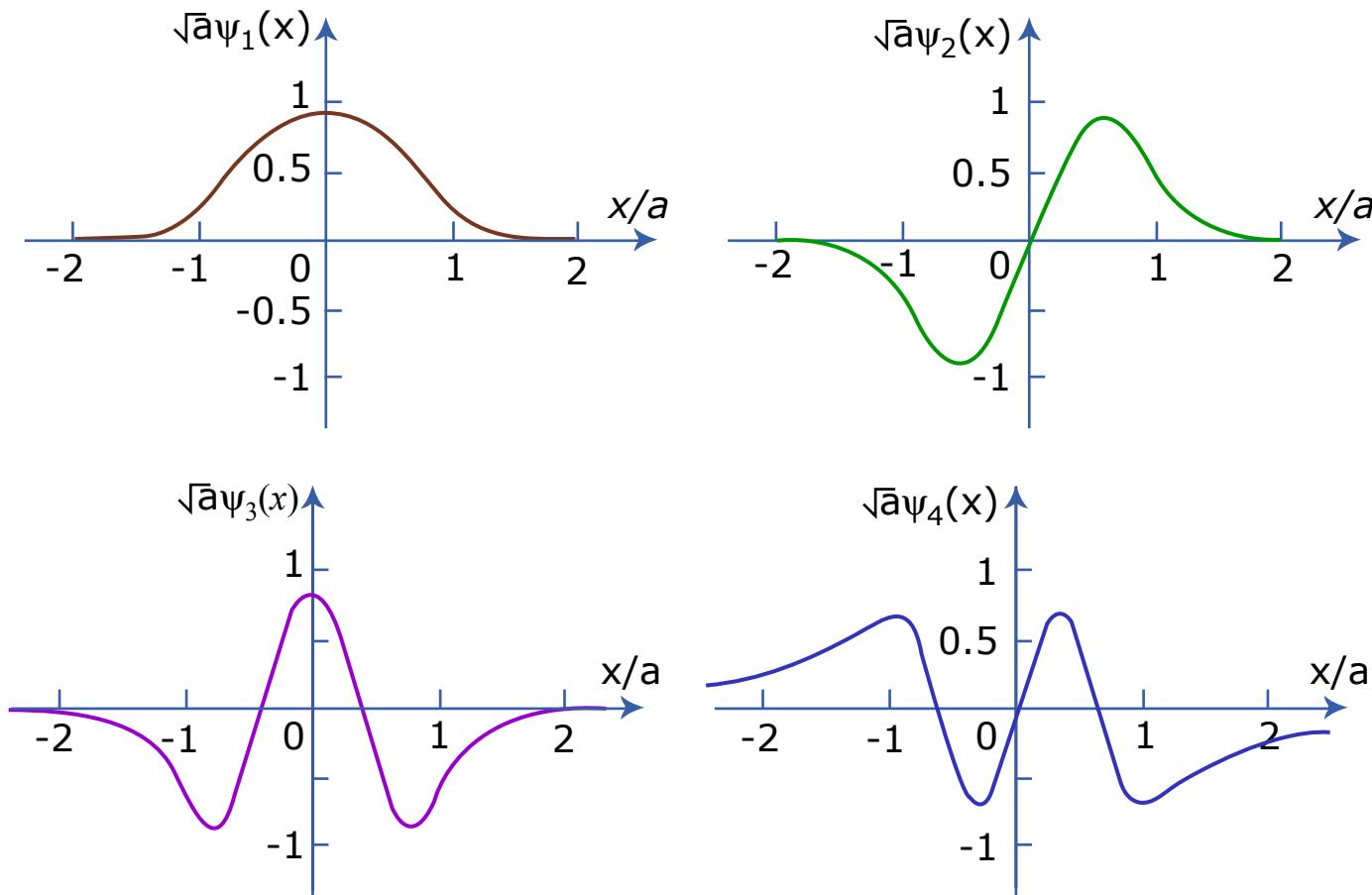
A Central Potential (e.g. the Nucleus)

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

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

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

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

Solutions in a Coulomb Potential: the Periodic Table

http://www.orbitals.com/orb/orbtable.htm
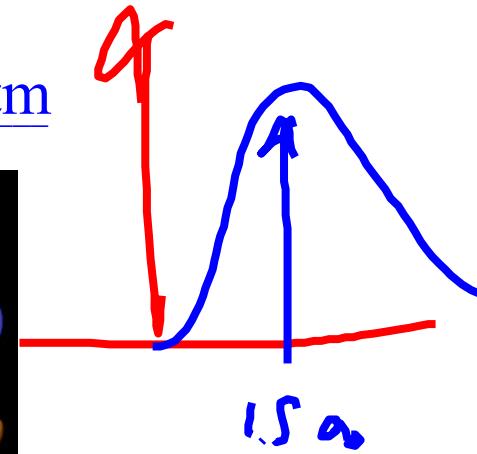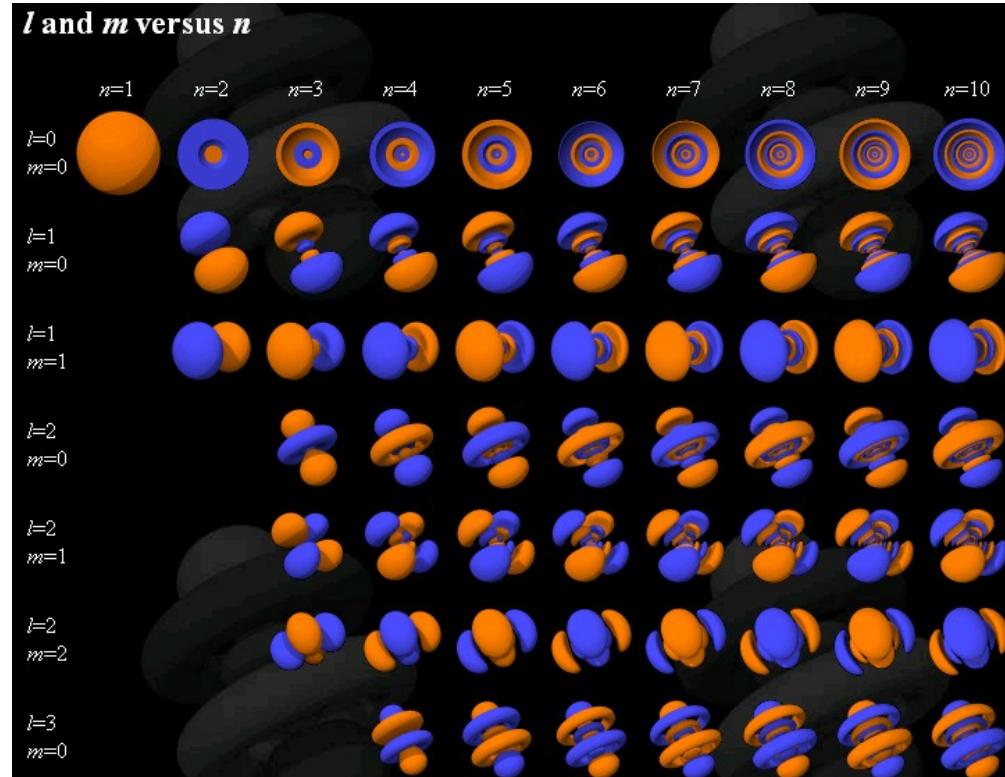
Courtesy of David Manthey. Used with permission.

Orthogonality, Expectation Values, and Dirac's <bra|kets>

$$\psi = \psi(\vec{r}) = |\psi\rangle$$

$$\int \|\psi(\vec{r})\|^2 = 1$$

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

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

Matrix Formulation (I)

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \quad \Leftrightarrow \quad \hat{H}|\psi\rangle = E|\psi\rangle$$

$$|\psi\rangle = \sum_{n=1,k} c_n |\varphi_n\rangle \qquad \{|\varphi_n\rangle\} \text{ k orthogonal functions}$$

$$\langle \varphi_m |\hat{H}|\psi\rangle = E\langle \varphi_m |\psi\rangle$$

$$\sum_{n=1,k} c_n \langle \varphi_m |\hat{H}| \varphi_n\rangle = Ec_m$$

$$\varphi_m^* \qquad \int d\vec{r}$$

$$\int d\vec{r}\, \varphi_m^* \sum_n c_n \psi_n$$

Matrix Formulation (II)

$$\sum_{n=1,k} c_n \langle \varphi_m | \hat{H} | \varphi_n \rangle = E c_m$$

$$\sum_{n=1,k} H_{mn} c_n = E c_m$$

$$\begin{pmatrix} H_{11} & \cdots\cdots & H_{1k} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ H_{k1} & \cdots\cdots & H_{kk} \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix}$$

Variational Principle

$$\int d\vec{r} \, \phi^* \hat{H} \phi$$

$$E[\Phi] = \frac{<\Phi \, | \, \hat{H} \, | \, \Phi>}{<\Phi \, | \, \Phi>}$$

$$E[\Phi] \geq E_0 \qquad \int \phi^* \phi$$

If $E[\Phi] = E_0$, then Φ is the ground state wavefunction, and viceversa…

$$|\phi\rangle = \sum c_n |\xi_n\rangle$$

$$H|\xi_n\rangle = \varepsilon_n |\xi_n\rangle$$

Energy of an Hydrogen Atom

$$E_\alpha = \frac{\langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle}$$

$$\Psi_\alpha = C \exp\left(-\alpha r\right)$$

$$\langle \Psi_\alpha | \Psi_\alpha \rangle = \pi \frac{C^2}{\alpha^3}, \qquad \langle \Psi_\alpha | -\frac{1}{2} \nabla^2 | \Psi_\alpha \rangle = \pi \frac{C^2}{2\alpha} \qquad \langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle = -\pi \frac{C^2}{\alpha^2}$$

Two-electron atom

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

Many-electron atom

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1, ..., \vec{r}_n) = E_{el}\psi(\vec{r}_1, ..., \vec{r}_n)$$

Energy of a collection of atoms

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

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

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

Electrons and Nuclei

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

- 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

- Adiabatic means that there is no coupling between different electronic surfaces; B-O no influence of the ionic motion on one electronic surface.

Complexity of the many-body Ψ

"…Some form of approximation is essential, and this would mean the construction of tables. The tabulation function of one variable requires a page, of two variables a volume and of three variables a library; but the full specification of a single wave function of neutral iron is a function of 78 variables. It would be rather crude to restrict to 10 the number of values of each variable at which to tabulate this function, but even so, full tabulation would require 10^{78} entries."

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

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 the product of single orbitals (i.e. we are working with independent electrons)

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

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

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

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

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

Differential Analyzer
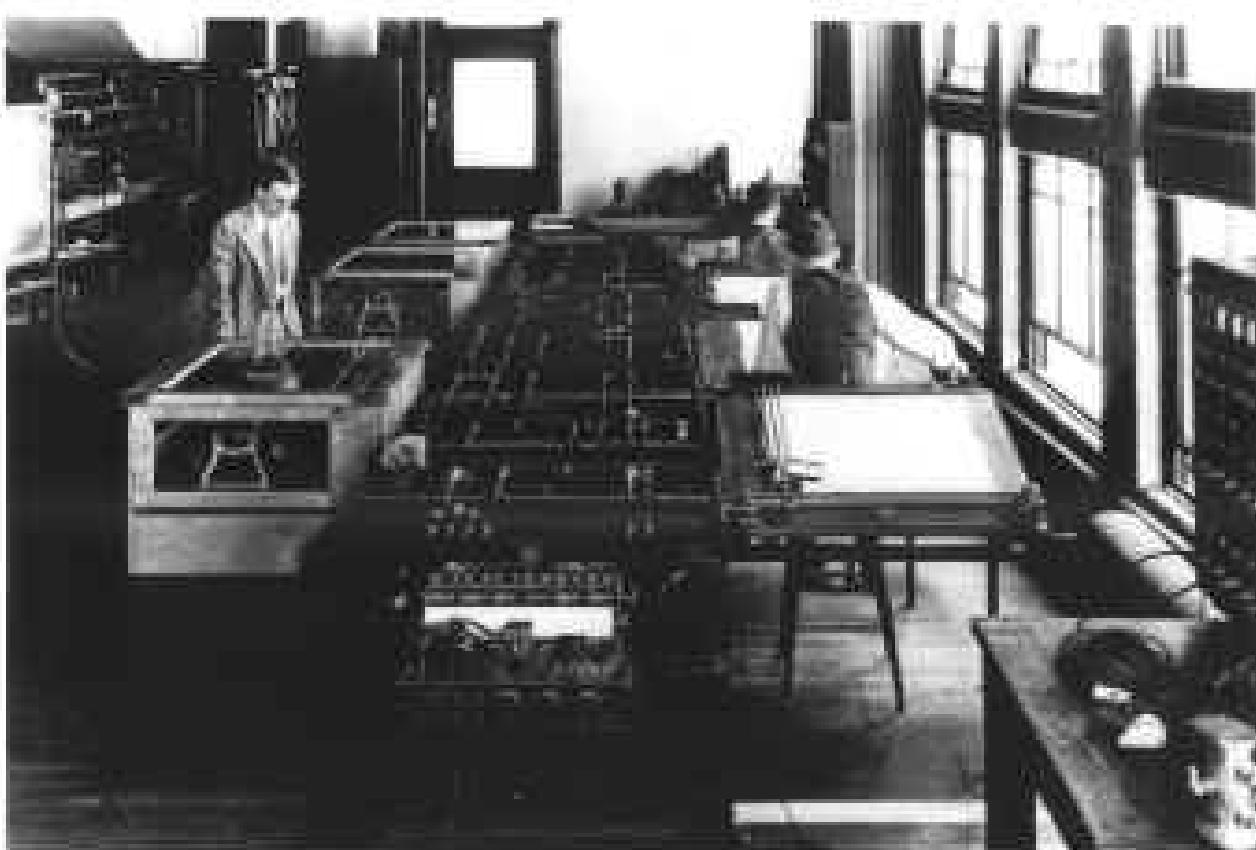
Vannevar Bush and the Differential Analyzer.
Courtesy of the MIT Museum. Used with permission.

What's missing

- It does not include correlation

- The wavefunction is not antisymmetric

- It does remove nl accidental degeneracy of the hydrogenoid atoms

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

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

- 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)

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

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

$$\psi(\vec{r}_1,...,\vec{r}_n) = \left\| Slater \right\|$$

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

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

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

Shell structure of atoms

- Self-interaction free

- Good for atomic properties

- Start higher-order perturbation theory

- Exchange is in, correlation still out

Faster, or better

- The exchange integrals are the hidden cost (fourth power). Linear-scaling efforts underway

- Semi-empirical methods (ZDO, NDDO, INDO, CNDO, MINDO): neglect certain multi-center integrals

- Configuration interaction, Møller-Plesset

Restricted vs. Unrestricted

- Spinorbitals in the Slater determinant: spatial orbital times a spin function

- Unrestricted: different orbitals for different spins

- Restricted: same orbital part

Koopmans' Theorems

- Total energy is invariant under unitary transformations

- It is not the sum of the canonical MO orbital energies

- Ionization energy, electron affinity are given by the eigenvalue of the respective MO, in the frozen orbitals approximation

Atomic Units and Conversion Factors (see handout)

1 a.u. = 2 Ry = 1 Ha

1 Ry = 13.6057 eV

1 eV = 23.05 kcal/mol

Software

- Gaussian (http://www.gaussian.com)
- Crystal (http://www.cse.clrc.ac.uk/cmg/CRYSTAL/, http://www.theochem.unito.it/)

References

- F. Jensen, *Introduction to Computational Chemistry*

- J. M. Thijssen, *Computational Physics*

- B. H. Bransden and C. J. Joachim, *Quantum Mechanics,* and also *Physics of Atoms and Molecules*