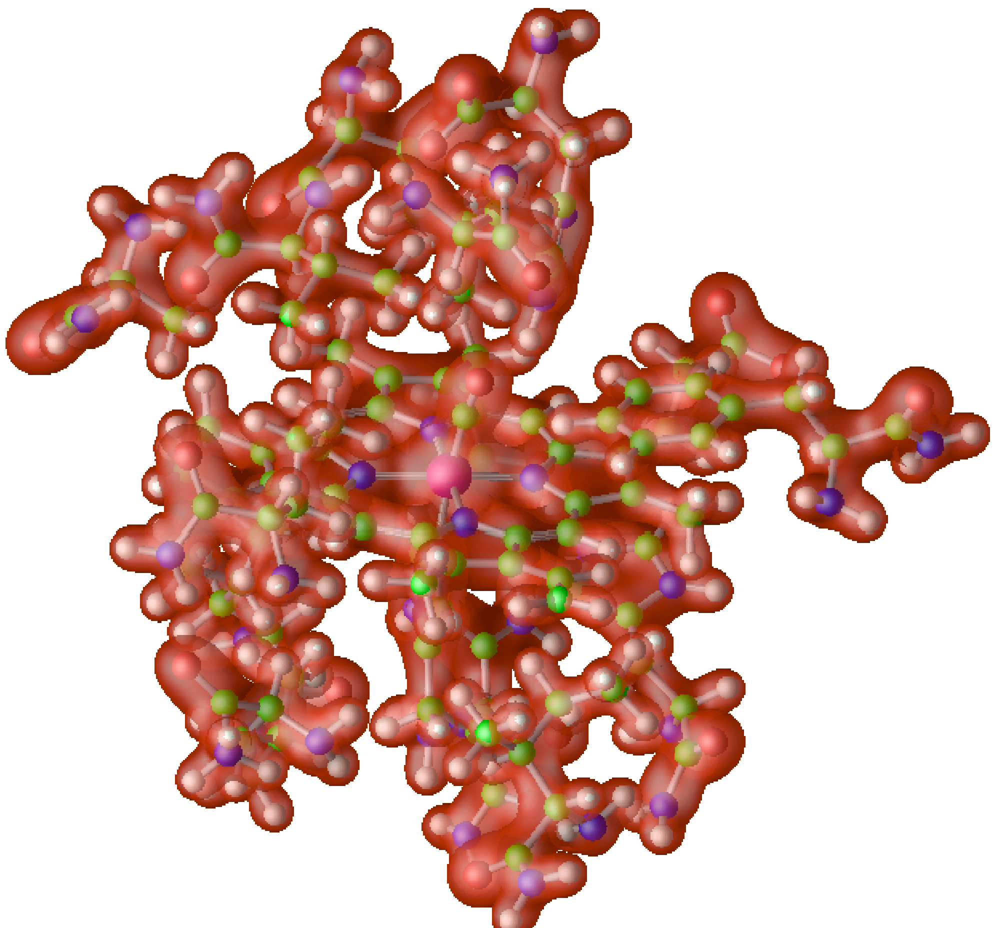
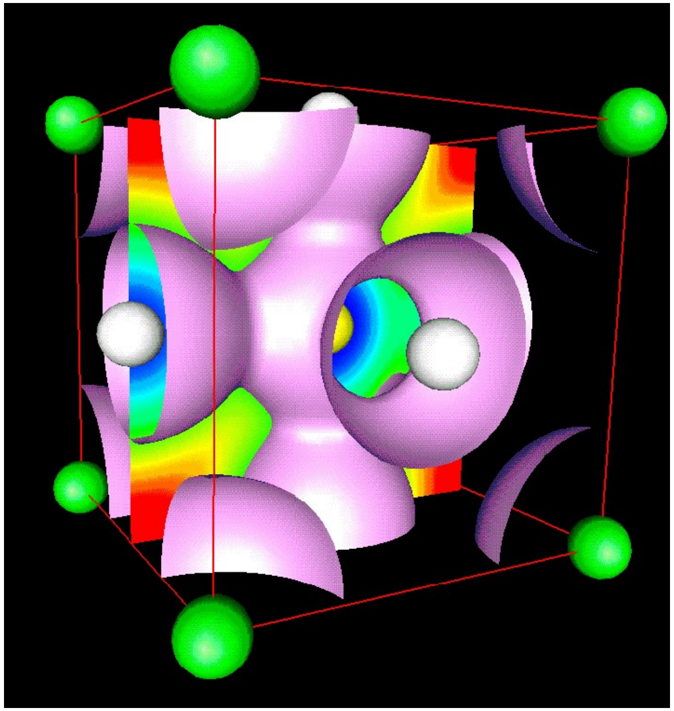
3.320: Lecture 3b (Feb 8 2005)

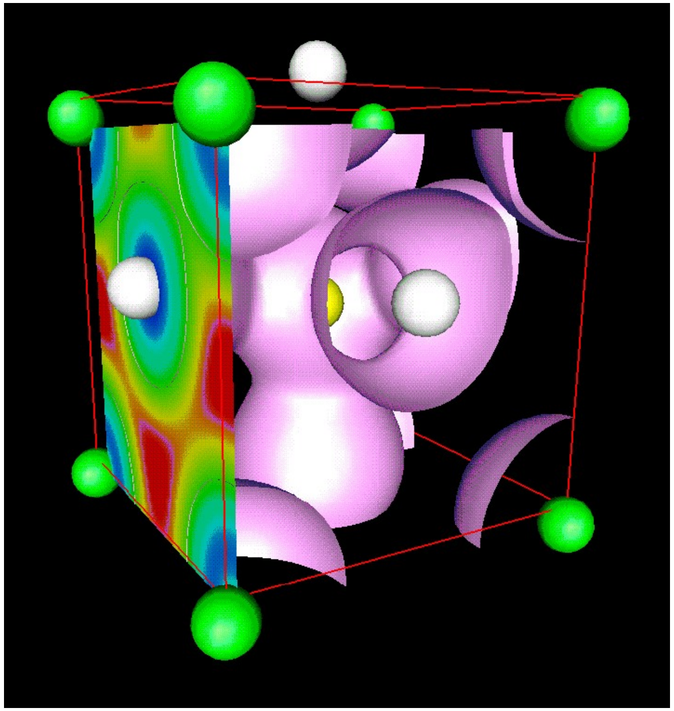
IT'S A QUANTUM WORLD !



Why do we need quantum mechanics ?

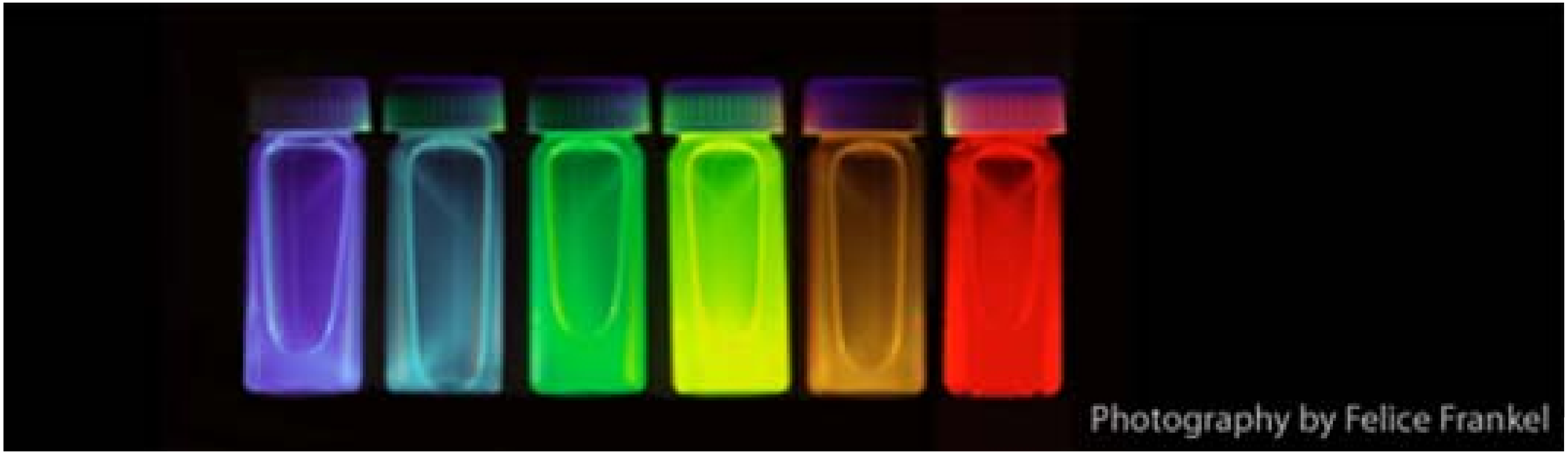
1) Bonding and Structure





Paraelectric (cubic) and ferroelectric (tetragonal) phases of $PbTiO_3$

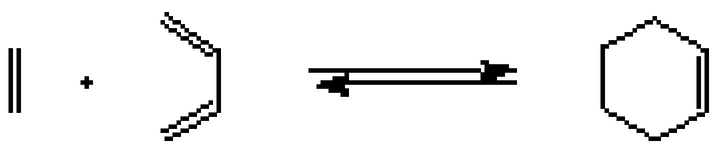
2) Electronic, optical, magnetic properties



3) Dynamics, chemistry

Diels-Alder Reaction:

1,3-butadiene + ethylene → cyclohexene



http://www.wag.caltech.edu/home-pages/jim/

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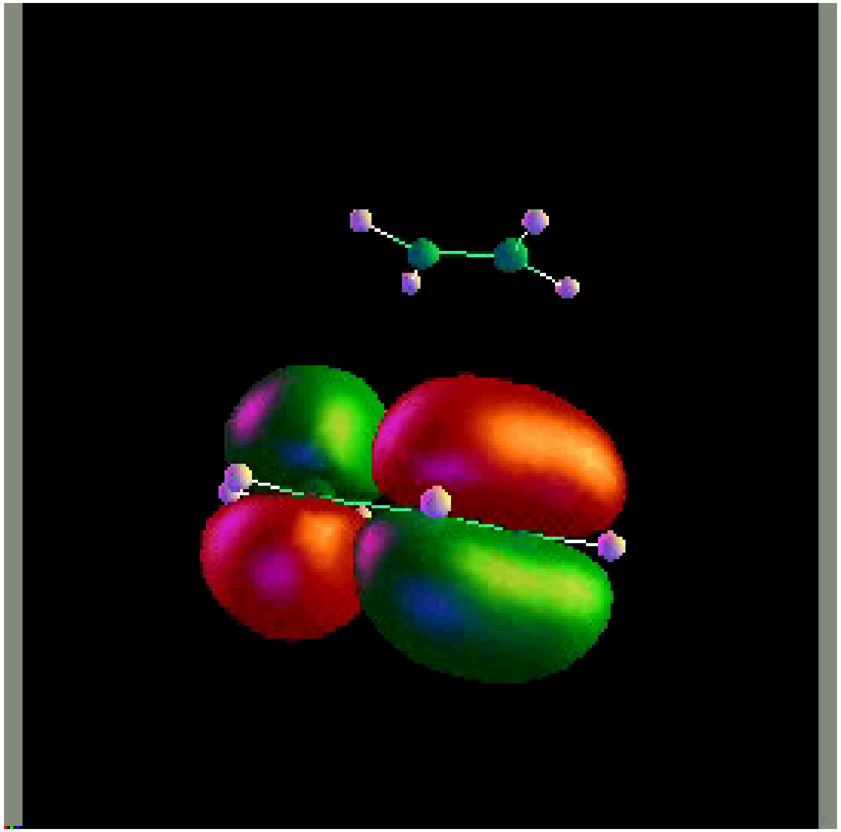
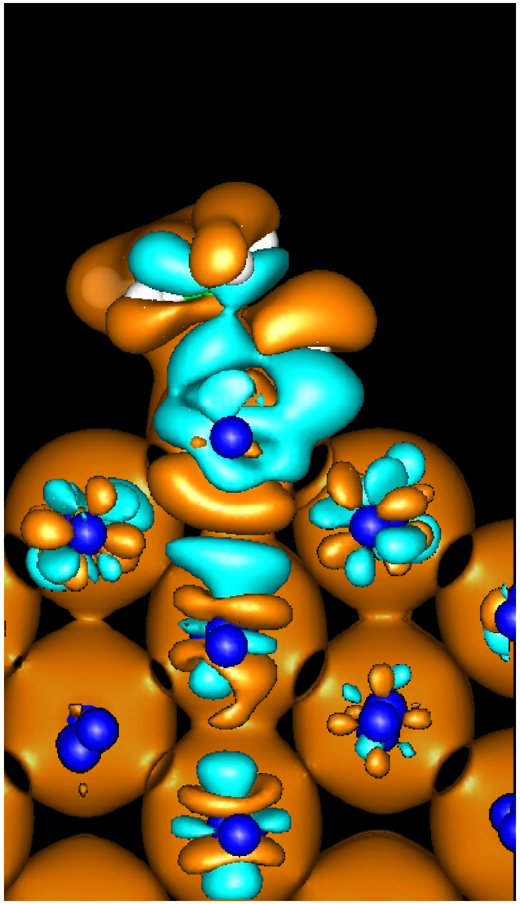


Standard Model of Matter

- Atoms are made by massive, point-like nuclei (protons+neutrons)
- Surrounded by tightly bound, rigid shells of core electrons
- Bound together by a glue of valence electrons



Material Properties From First-Principles

- Energy at our living conditions (300 K): 0.04 eV (kinetic energy of an atom in an ideal gas: 3/2 $k_B T$).
- Differences in bonding energies are within one order of magnitude of 0.29 eV (hydrogen bond).
- Binding energy of an electron to a proton (hydrogen):
  13.6058 eV = 1 Rydberg (Ry) = 0.5 Hartree (Ha) = 0.5 a.u

Bibliography

- Richard M. Martin, *Electronic Structure: Basic Theory and Practical Methods,* Cambridge University Press (2004).
- Mike Finnis, *Interatomic Forces in Condensed Matter*, Oxford University Press (2003).
- Efthimios Kaxiras, *Atomic and Electronic Structure of Solids*, Cambridge University Press (2003).

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Wave-particle Duality

- *Waves have particle-like properties:*
  - *Photoelectric effect: quanta (photons) are exchanged discretely*
  - *Energy spectrum of an incandescent body looks like a gas of very hot particles*
- Particles have wave-like properties:
  - Electrons in an atom are like standing waves (harmonics) in an organ pipe
  - Electrons beams can be diffracted, and we can see the fringes

When is a particle like a wave ?

Wavelength • momentum = Planck

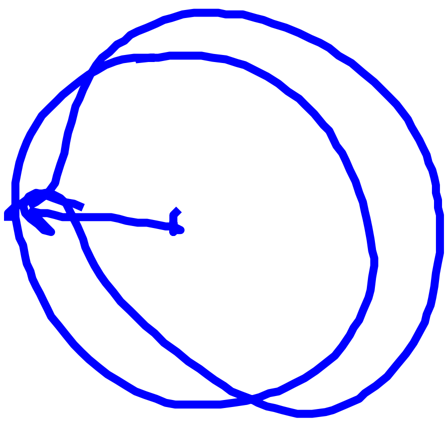
$$\lambda \cdot p = h$$

(h = 6.6 x 10^{-34} J s)

$m_e v_{is}$ 2π

http://www.kfunigraz.ac.at/imawww/vqm/

0.53 Å



Quantum effects in the nuclear motion

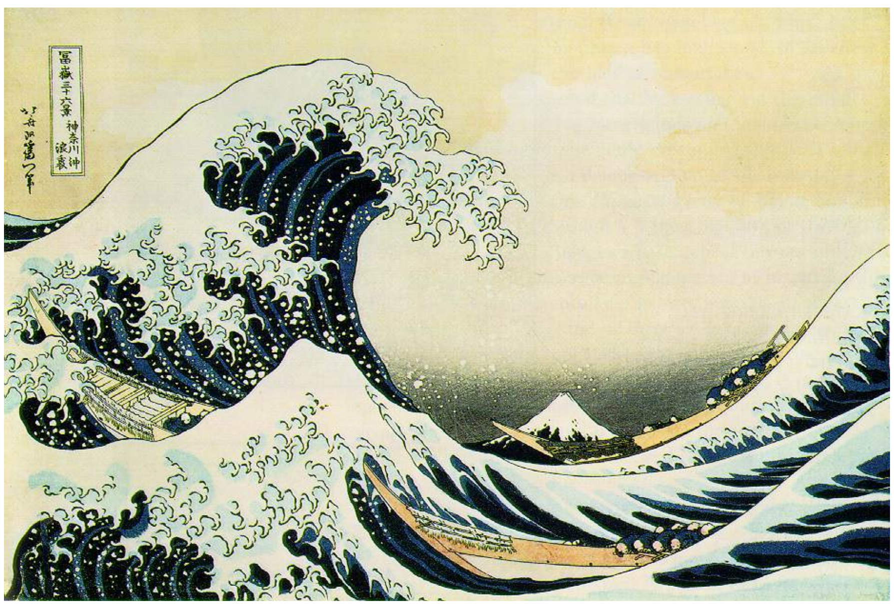
"The nature of the hydrated excess proton in water", Marx, D., Tuckermann, M. E., Hutter, J., & Parrinello, M. (1999). Nature (London) 397, 601-604

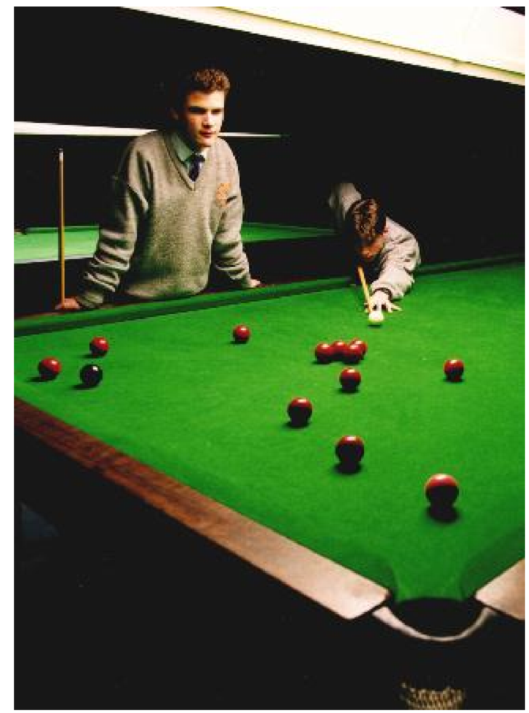
Pair of graphs removed for copyright reasons.
Source: Marx et al, Nature 1999 as above.

"Effect of Quantum Fluctuations on Structural Phase Transitions in $SrTiO_3$ and $BaTiO_3$", W. Zhong and David Vanderbilt, Phys.Rev. B 53, 5047 (1996)

So, What Is It ? A Misnomer…

It's the mechanics of waves, instead of classical particles





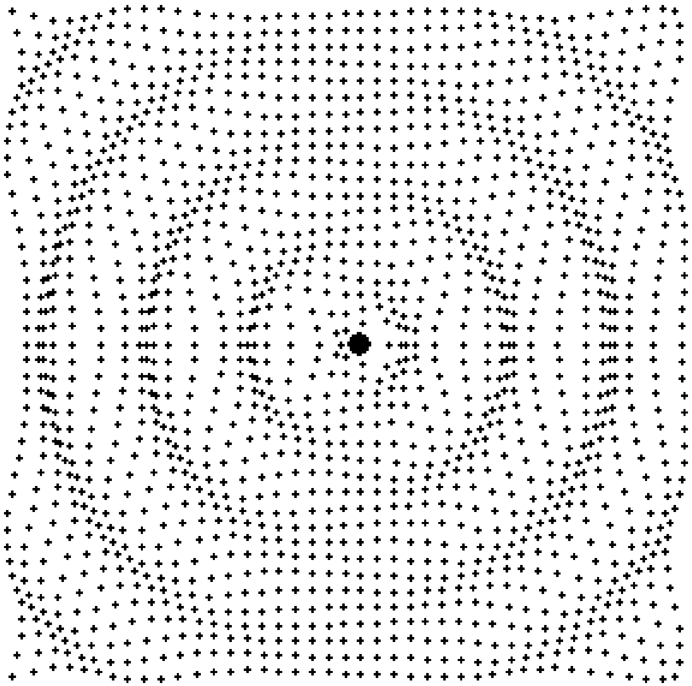
Mechanics of a Particle

$$m\frac{d^2\vec{r}}{dt^2} = \vec{F}(\vec{r}) = -\vec{\nabla}V(\vec{r}) \longrightarrow \begin{matrix}\vec{r}(t) \\ \vec{v}(t)\end{matrix}$$

The sum of the kinetic and potential energy is conserved

Image removed for copyright reasons.
Cannon firing a cannonball.

Description of a Wave



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

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

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)

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

Stationary Schrödinger's Equation (II)

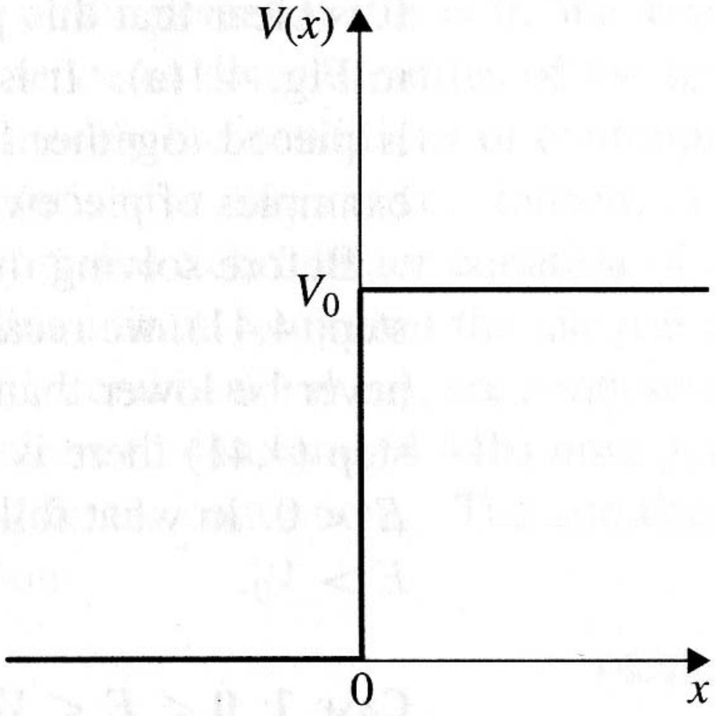
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\varphi(\vec{r}) = E\varphi(\vec{r})$$

Interpretation of the Quantum Wavefunction (Copenhagen)

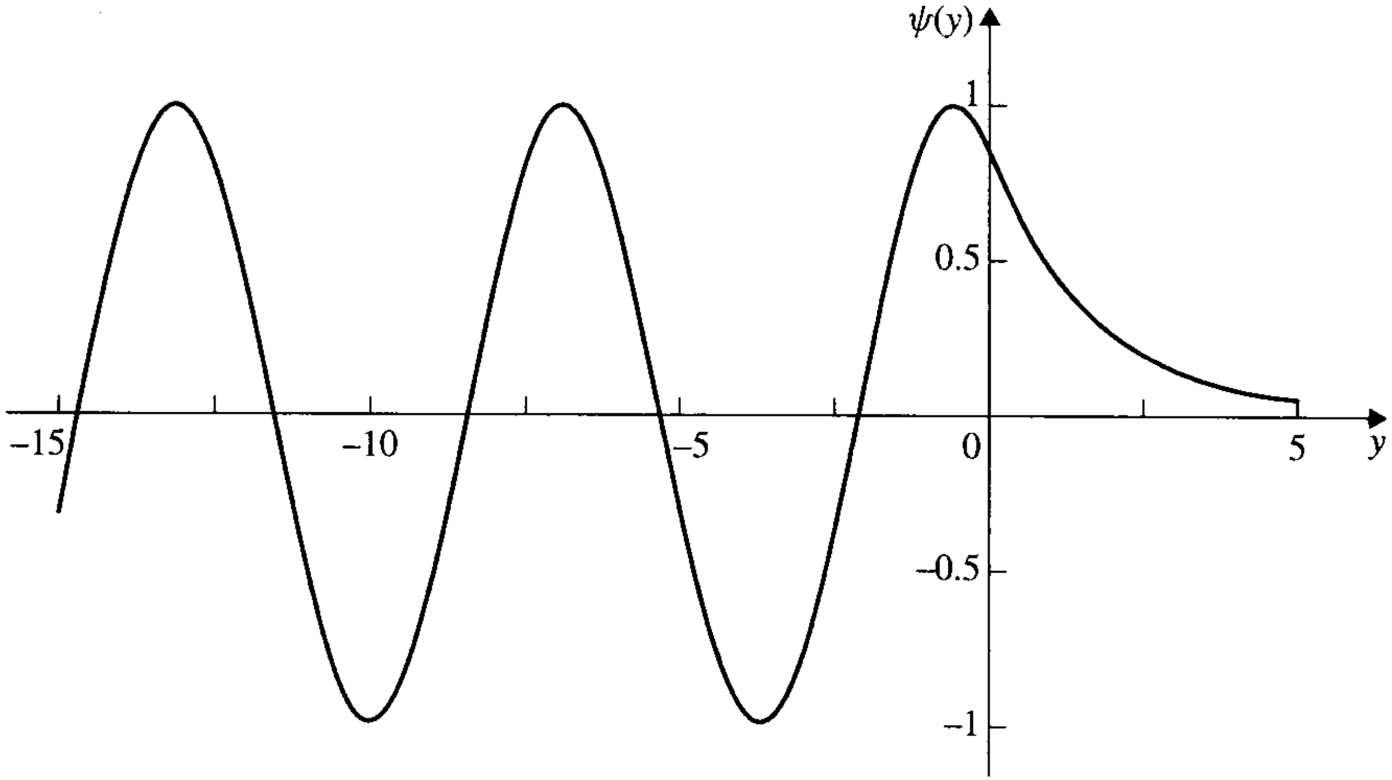
$$\left\| \Psi(\vec{r}, t) \right\|^2$$ is the probability of finding an electron in *r* and *t*

$$\left\| \varphi(\vec{r}) \exp\left(-\frac{i}{\hbar} E t\right) \right\|^2 = \left\| \varphi(\vec{r}) \right\|^2$$

Metal Surfaces (I)



Metal Surfaces (II)



Solutions in a Coulomb Potential: the Periodic Table

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