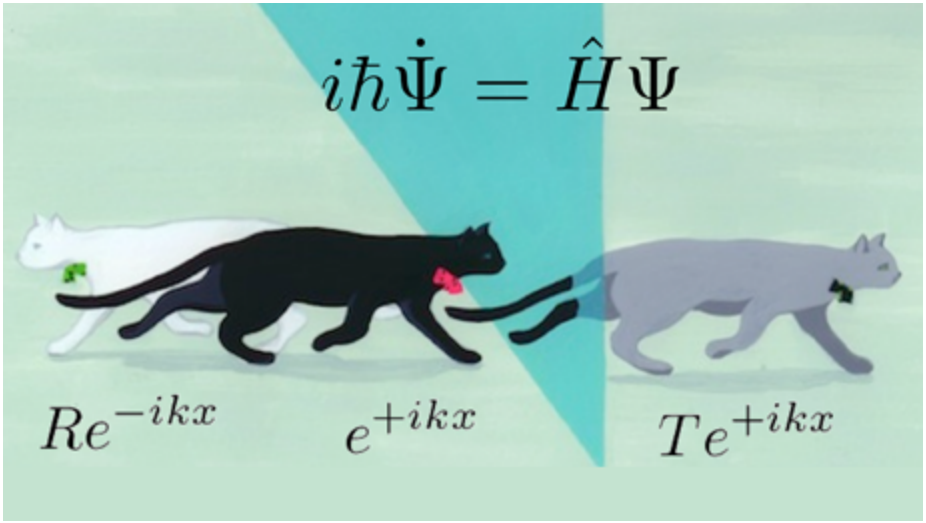
Exploring Quantum Physics

Coursera, Spring 2013 Instructors: Charles W. Clark and Victor Galitski

Solving the Schrödinger Equation

Part II. Gaussians and the Variational Theorem



Solving the Schrödinger Equation

Stationary States – a Constructive Approach

We concluded last time with a construction of *E and* V for one of the most widely-used functions in quantum mechanics.

$$\Psi(x,y,z) = \frac{1}{\pi^{3/4} d^{3/2}} \exp\left[-\frac{x^2+y^2+z^2}{2d^2}\right]$$

You saw the one-dimensional version of this in Victor's lectures on the harmonic oscillator last week. Here is the notation I prefer:

$$\Psi(x) = \frac{1}{\pi^{1/4} d^{1/2}} \exp\left[-\frac{x^2}{2d^2}\right] \qquad d = \sqrt{\frac{\hbar}{m\omega}}$$

Since *d* appears in the exponent, it must have the dimensions of length, [L].

Solving the Schrödinger Equation

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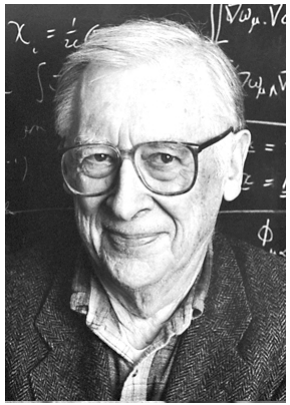

John A. Pople
1925-2004
1998 Nobel Prize in Chemistry
"for his development of computational methods in quantum chemistry".

The Gaussian Workhorse

$$\Psi(x,y,z) = \frac{1}{\pi^{3/4} d^{3/2}} \exp\left[-\frac{x^2+y^2+z^2}{2d^2}\right]$$

Self—consistent molecular orbital methods. XII. Further extensions of gaussian—type **basis sets** for use in molecular orbital studies of organic molecules
WJ Hehre, R Ditchfield, JA Pople - The Journal of Chemical Physics, 1972 - link.aip.org
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Gaussian **basis sets** for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen
TH Dunning Jr - The Journal of Chemical Physics, 1989 - link.aip.org
In the past, **basis sets** for use in correlated molecular calculations have largely been taken from single configuration calculations. Recently, Almlöf, Taylor, and co-workers have found that **basis sets** of natural orbitals derived from correlated atomic calculations (ANOs) ...
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It seems likely that more work using quantum mechanics is done by chemists rather than physicists!

Solving the Schrödinger Equation

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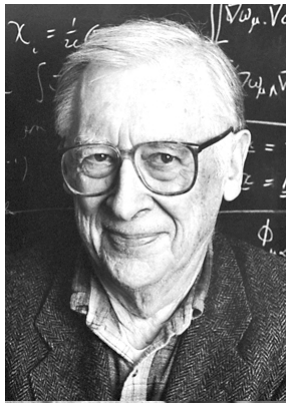

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A model of leptons
S **Weinberg** - Physical Review Letters, 1967 - APS
The condition that p, have zero vacuum expec-tation value to allorders of perturbation theory tells us that A.'—= M,'/2h, and therefore the field p, has mass M, while p, and p have mass zero. But me can easily see that the Goldstone bosons represented by y, and y have no ...
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The most-cited paper in physics!

Solving the Schrödinger Equation

The Gaussian Workhorse: the Variational Theorem

For any Hamiltonian $\hat{H}$ and for any function Ψ for which $< \Psi | \Psi >= 1$, we have

$$< \Psi | \hat{H} | \Psi > \geq E_0$$

Thus we can use convenient sets of “trial functions” to estimate the ground-state energy of a system.

Solving the Schrödinger Equation

The Gaussian Workhorse: the Variational Theorem

For any Hamiltonian $\hat{H}$ and for any function Ψ for which $< \Psi | \Psi >= 1$, we have

$$< \Psi | \hat{H} | \Psi > \geq E_0$$

$$\Psi = \sum_n |\Phi_n >< \Phi_n | \Psi > \qquad \hat{H} | \Phi_n >= E_n | \Phi_n >$$

$$< \Psi | \hat{H} | \Psi >= \sum_{n,m} < \Psi | \Phi_m >< \Phi_m | \hat{H} | \Phi_n >< \Phi_n | \Psi >$$

$$= \sum_n < \Psi | \Phi_n > E_n < \Phi_n | \Psi > \geq \sum_n < \Psi | \Phi_n > E_0 < \Phi_n | \Psi >= E_0$$

Solving the Schrödinger Equation

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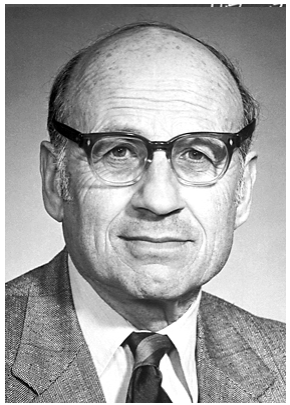

Walter Kohn
1923-
1998 Nobel Prize in Chemistry
"for his development of the density-functional theory“.

Why this is important

Electrons are the glue that holds materials together.

To find the equilibrium positions of nuclei in molecules or solids, you minimize the total energy of the system. For many cases of practical interest, this can be done by solving the Schrödinger equation for E_0 at fixed values of nuclear coordinates, then vary those coordinates to minimize E_0 (Born-Oppenheimer approximation).

Solving the Schrödinger Equation

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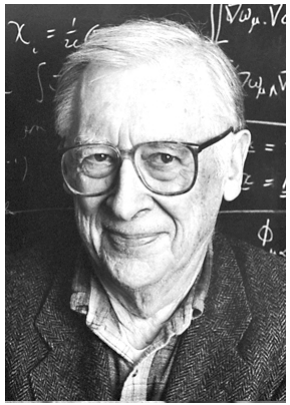

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Gaussian orbitals are extremely convenient in large-scale calculations:

Simplify multi-center integrals
Compact, computationally efficient