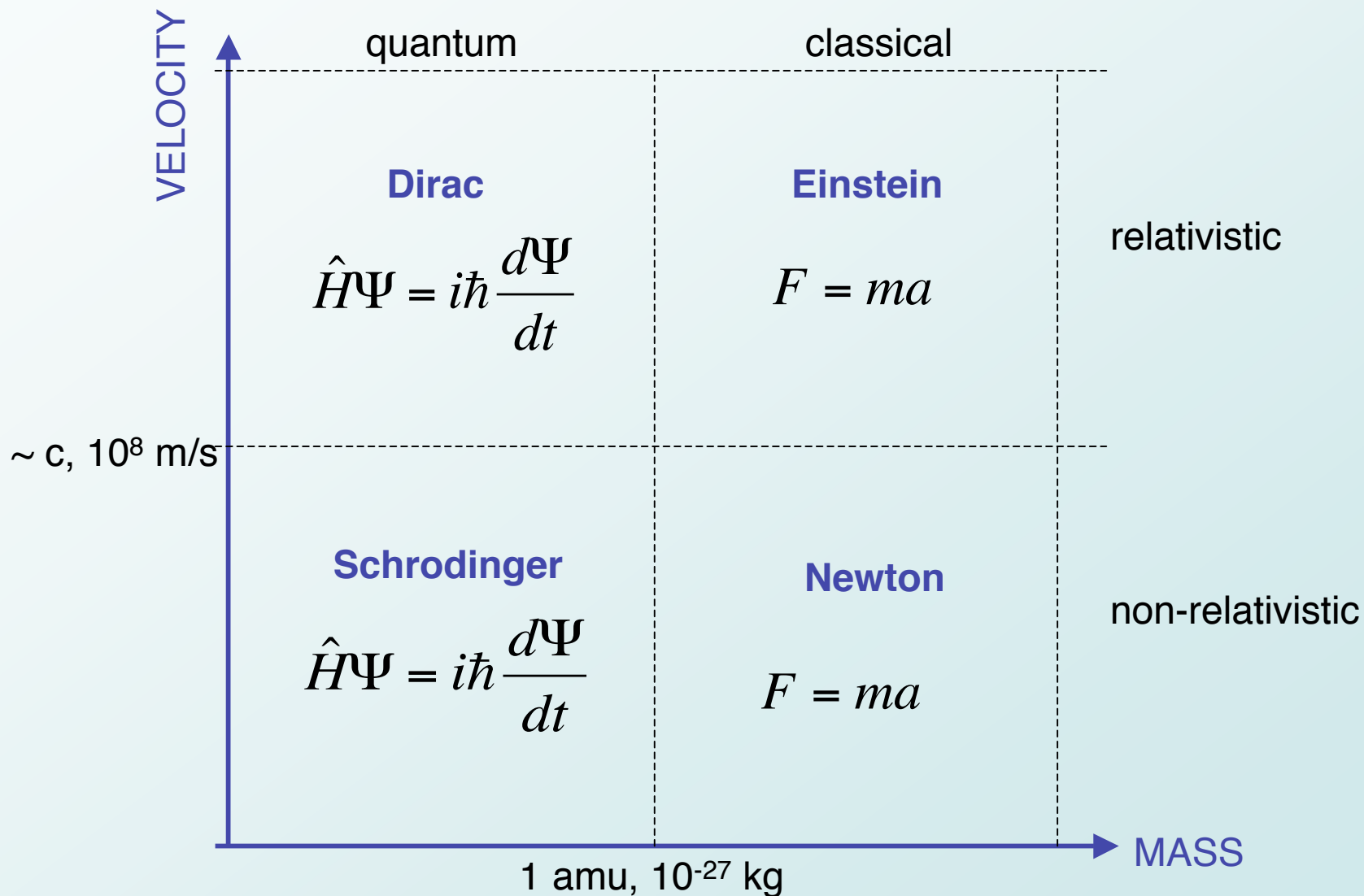


Computational Nanoscience
NSE C242 & Phys C203
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Lecture 13:
Intro to Computational Quantum Mechanics
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The Dynamical Equations



After Jensen, 2007.

A Little Bit of Schrödinger

Now that we've done everything we can to **avoid** using quantum mechanics, let's take a look at what we've been avoiding.

What is the central difference between a quantum mechanical simulation and one using classical potentials?

The starting point for any discussion on quantum mechanics is, of course, the Schrödinger equation:

$$\hat{H}\Psi = i\hbar \frac{d\Psi}{dt}$$

Hamiltonian Operator

$$\hat{H} = \hat{T} + \hat{V} = KE + PE$$

$\Psi(\mathbf{r}, t)$
wavefunction

Written out explicitly, the Schrödinger equation looks like this:

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right\} \Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$

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- $\Psi(\mathbf{r}, t)$ is the wavefunction for the system of particles, which for now we will assume is normalized. It characterizes the particle's motion. One can derive all properties of the system of particles from its wavefunction.
- We no longer ask “Where is/are the particle(s)?”, but instead ask “What is the probability distribution governing the positions?”

$$1 = \int P(r, t) dr = \int dr \Psi^*(r, t) \Psi(r, t) = \int dr |\Psi(r, t)|^2$$

A Little Bit of Schrödinger

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right\} \Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$

This equation describes a single particle, like an electron, of mass m which is moving through space and time under the influence of an external potential V .

When the external potential is independent of time then the wavefunction can be written as the product of a spatial part and a time part.

This allows us to write down time-independent version of the Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V \right\} \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

Where ∇^2 is the usual second derivative operator.

A Little Bit of Schrödinger

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V \right\} \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

To solve this equation one must find values of E and functions Ψ such that when the wavefunction is operated on by the Hamiltonian, it returns the wavefunction multiplied by the energy.

The Schrödinger equation is a partial differential eigenvalue equation - a broad class of equations in which an operator acts on a function (eigenfunction) and returns the function multiplied by a scalar (eigenvalue).

Here's a simple example of an eigenvalue equation: $\frac{d}{dx}(y) = ry$

What is an eigenfunction for this equation?

A simple second order equation (as is the S.Eq.) is: $\frac{d^2 y}{dx^2} = ry$

Quantum Mechanics - Four Postulates (Liboff)

(1) For each observable, there exists an operator. Measurement of the observable yields an eigenvalue of that operator.

$$\hat{A}\phi(r) = \tilde{\phi}(r)$$

operator

$$\hat{A}\phi_a(r) = a\phi_a(r)$$

eigenvalue

eigenfunction

Examples of operators for single particle systems:

momentum $\hat{p}\phi(r) = -i\hbar\nabla\phi(r)$ is three equations

x momentum $\hat{p}_x\phi(r) = -i\hbar\frac{\partial}{\partial x}\phi(r)$

kinetic energy $\hat{T}\phi(r) = \frac{\hat{p} \cdot \hat{p}}{2m}\phi(r) = -\frac{\hbar^2}{2m}\nabla^2\phi(r)$

total energy $(\hat{T} + \hat{V})\phi(r) = \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(r) \right] \phi(r)$

Quantum Mechanics - Four Postulates (Liboff)

(2) A measurement of an observable “A” yielding the eigenvalue “a” leaves the particle in the eigenstate $\phi_a(r)$.

(3) The expected value of a measurement of an observable is

$$\langle A \rangle = \int dr \Psi^*(r, t) \hat{A} \Psi(r, t)$$

* these are weighted averages only, i.e., the expectation may not be an eigenvalue itself

(4) The Schrodinger equation governs the evolution of the wavefunction.

$$\hat{H}\Psi = i\hbar \frac{d\Psi}{dt}$$

Operators

Everything we could possibly care to know about the system is contained in the wavefunction. In particular, we can compute the expectation value for any observable

$$\langle A \rangle = \int dr \Psi^*(r,t) \hat{A} \Psi(r,t)$$

In quantum mechanics, the expectation value (i.e., average value) of a quantity such as energy, position, linear momentum, etc., can be determined using the appropriate operator.

for example $\langle p_x \rangle = \int dr \Psi^*(r,t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(r,t)$

What's the operator for the energy (most common one)?

$$\langle E \rangle = \int \Psi^* \hat{H} \Psi d\mathbf{r}$$

The Hamiltonian can typically be broken up into kinetic and potential energy operator terms:

$$K = -\frac{\hbar^2}{2m} \nabla^2 \quad V = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (\text{e.g., for a single electron interacting with a nucleus with } Z \text{ protons})$$

Quantum Mechanics - Basic Approach

- “Solving” the Schrodinger equation refers writing down the Hamiltonian for the system of interest, and then determining the eigenvalues and eigenfunctions
- This usually boils down to solving a matrix system of equations
- We choose a set of orthonormal basis functions (just some basis) to expand the eigenstates

$$|\Psi\rangle = \sum_{n=1}^N c_n |\phi_n\rangle$$

- Then, the Schrodinger equations turns into a matrix system:

$$[(\underline{\underline{H}} - \varepsilon \underline{\underline{I}})]\{\underline{\underline{c}}\} = 0$$

- We can diagonalize the matrix $\underline{\underline{H}}$ to determine the eigenvalues ε and the eigenfunctions $\{\underline{\underline{c}}\}$
- As an example, we will do this first for hydrogen, and then look at what happens as we increase the number of particles in the system

Units

Usually we try to make units easy to manage in the simulation. Atomic units provide a natural way to scale the basic units.

- 1 unit of **charge** = absolute charge on an electron = 1.60219×10^{-19} C
- 1 **mass** unit = mass of an electron = 9.10593×10^{-31} kg
- 1 unit of **length** (1 Bohr) = 5.29177×10^{-11} m
- 1 unit of **energy** (1 Hartree) = 4.35981×10^{-18} J

A couple of observations:

- 1 Bohr = the radius of the first orbit in Bohr's treatment of the H atom, about half an Angstrom
- 1 Hartree = the interaction between two electronic charges separated by 1 Bohr, 1 Hartree \sim 27 eV
- The total energy of the 1s electron in the H atom is -0.5 Hartree

Exact Solutions to Schrödinger Equation

Are not really all that interesting!

Only a few problems can be solved exactly, such as the particle in a box, the harmonic oscillator, the particle on a sphere, the hydrogen atom.

These are all solved in elementary quantum mechanics textbooks. Boundary conditions are imposed, etc.

One important thing that you would do in solving these problems is to make sure that the wavefunction is both normalized and orthogonal.

This means: $\int \Psi^* \Psi d\mathbf{r} = 1$ and $\int \Psi_m^* \Psi_n d\mathbf{r} = \delta_{mn}$

It's Nice to Start with the Hydrogen Atom

In atomic units, the Hamiltonian for an electron in the Hydrogen atom is:

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

For the hydrogen atom, $Z=+1$, for the He^+ atom, $Z=+2$ and so on.

From here, one usually transforms the equation to polar coordinates.

Then, the solution can be written in terms of a product of the radial function $R(r)$ and an angular function $Y(\theta, \varphi)$.

$$\Psi_{nlm} = R_n(r)Y_{lm}(\theta, \varphi)$$

The wavefunctions are commonly referred to as orbitals and are characterized by three quantum numbers n , l , and m .

- n is the principle quantum number: 0, 1, 2, ...
- l is the azimuthal quantum number: 0, 1, ... ($n-1$)
- m is the magnetic quantum number: $-l, -(l-1), \dots, 0, \dots, (l-1), l$

Quantum vs. Classical States

Let's take a brief step back at this point.

Remember that we used the Gibb's prescription to calculate thermal averages of a given physical quantity at a temperature T:

$$\langle \vartheta \rangle = \frac{\sum_s \exp(-\beta E_s) \vartheta(s)}{\sum_s \exp(-\beta E_s)}$$

Where the sum runs over all accessible states of system.

This prescription is very general and is not related to the type of physics governing the system, i.e., classical or quantum.

In classical physics, a state is defined by assigning positions and velocities (or equivalently momenta). Such a state has a well-defined energy:

$$E(state) = T + V = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i < j} v(\mathbf{r}_i, \mathbf{r}_j)$$

Quantum vs. Classical States

$$E(\text{state}) = T + V = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i < j} v(\mathbf{r}_i, \mathbf{r}_j)$$

Thus, because any classical state is also a state with a well-defined energy, the sum in this equation can be written as a sum over all classical states.

In other words, the sum is over all possible positions and momenta (velocities) of all of the particles.

In Quantum Mechanics this “luxury” is lost; it is impossible to specify at one time *both* position *and* momentum of a particle. The knowledge of one will automatically rule out the specification of the other.

More precisely, the more accurate the specification of, say, the position, the greater is the interval of variation of the momenta.

The impossibility of specifying, *with arbitrary accuracy*, both the position and the momentum of a particle is known as *Heisenberg uncertainty principle*.

$$\Delta x \Delta p \sim \hbar$$

Heisenberg

As, say the position comes to be known with greater and greater accuracy, i. e. as $\Delta x \rightarrow 0$, Δp can grow without bound.

Because $\Delta p^2 = \langle p^2 \rangle - \langle p \rangle^2$, then if Δp grows without bound even the *kinetic energy* of the particle, proportional to $\langle p^2 \rangle$, will grow without bound.

But, is it then possible to have a system with a well-defined total energy ?

The answer is yes, but such a state will also be characterized by the fact that *neither positions nor momenta* of any particle will be known exactly; rather, only their average values will be known.

It is possible to devise a formalism in which the state of the system is described by a function which contains all of the information that can be known about the system under examination.

And what would this function be??

Quantum vs. Classical

One of the fundamental differences between a quantum and classical description of particles is that in the quantum picture particles are delocalized.

This inherent delocalization of all the particles may be negligible for a particular system, depending on the temperature, the interparticle interaction and the particle mass.

At finite temperature, a convenient criterion can be formulated to establish how important a role quantum physics may play in determining the properties of a system, based on the concept of *thermal wavelength* of a particle.

The thermal wavelength Λ provides a measure of the region of space within which a particle of a given mass is *delocalized* by quantum effects.

$$\Lambda = \sqrt{2\lambda\beta}$$

with $\lambda = \hbar^2 / 2m$ and m being the mass of the particle.

Degree of Quanticity

$$\Lambda = \sqrt{2\lambda\beta}$$

This expression is of fundamental importance, as it should be always used to give a rough determination of the “degree of quanticity” of a given system.

To the extent that the thermal wavelength is small compared to a typical length associated with the problem under study, typically the distance over which the interparticle potential changes significantly, the system behaves classically.

Moreover, this equation tells us immediately that quantum effects generally become important at low temperatures, or for lighter particles, or for denser systems (where the short interparticle distance might become comparable to the interparticle separation).

Degree of Quanticity

Let's consider a few examples. First, liquid argon at a temperature of 80K and at its equilibrium density, corresponding to an interparticle distance of $\sim 5 \text{ \AA}$.

The thermal wavelength of an argon atom is approximately 1 \AA , and the Lennard-Jones potential describing the interaction between two Ar atom does not change too much between, say, 4 and 6 \AA .

Thus, we may conclude that the classical approximation is probably all right for liquid argon (in practice, there are nontrivial quantum corrections!).

As a second example, consider liquid helium at $T=4 \text{ K}$. The thermal wavelength of a helium atom is roughly 1.7 \AA , and the equilibrium density is 0.01873 particles per \AA^3 , corresponding to an interparticle separation of $\sim 3.76 \text{ \AA}$.

The helium-helium interparticle potential is to a good approximation a Lennard-Jones potential, with $\sigma=2.556 \text{ \AA}$.

Because this potential changes considerably in an interval centered at a distance 3.76 \AA and 1.7 \AA wide, quantum effects are likely to be important.

Degree of Quanticity

As a final example, let us consider an electron in a hydrogen atom at $T=300$ K, i. e. room temperature.

The thermal wavelength of an electron is roughly 10 \AA at this temperature, or about 20 times the Bohr radius (the radius of the orbit of the 1s electron in the hydrogen atom) and also significantly larger than most atom sizes.

Thus, *an electron in an atom cannot be considered a classical object* even at room temperature.

Back to the Hydrogen Atom

In atomic units, the Hamiltonian for an electron in the Hydrogen atom is:

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

For the hydrogen atom, $Z=+1$, for the He^+ atom, $Z=+2$ and so on.

From here, one usually transforms the equation to polar coordinates.

Then, the solution can be written in terms of a product of the radial function $R(r)$ and an angular function $Y(\theta, \varphi)$.

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Some Things

$$\Psi_{nlm} = R_n(r)Y_{lm}(\theta, \varphi)$$

A couple of things to note:

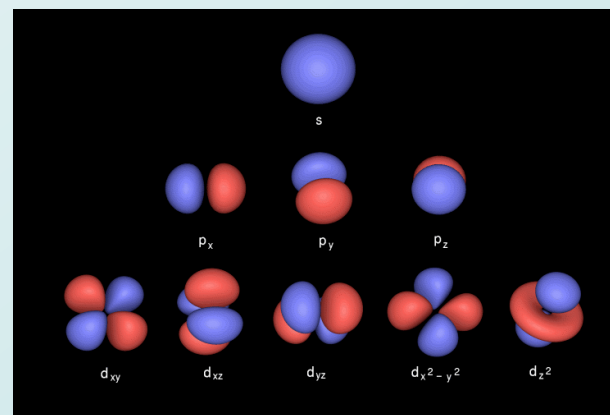
The solution for $R(r)$ and $Y(\theta, \varphi)$ can be derived analytically for a 1-electron - 1-nucleus system like the hydrogen atom.

The Energy is a function of the principle quantum number (n) only.

This means that orbitals with the same value of n but different values of l and m are “degenerate.”

Here are some pictures of atomic orbitals:

Note that each orbital is orthogonal to each other.



www.chemcomp.com/journal/molorbbs.htm

Multi-electron Atoms and Molecules

Are not solvable exactly*, as we have discussed. What happens as we go from the hydrogen case to a multiple particle, interacting system?

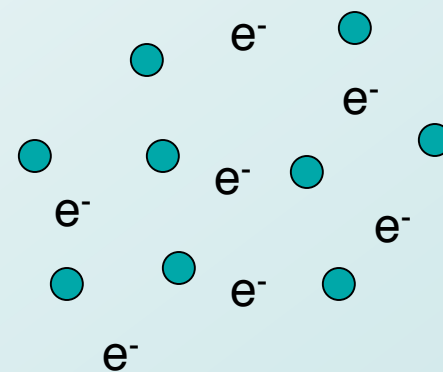
Given a collection of nuclei and electrons in some arrangement, what does the Hamiltonian look like?

Let R_1, \dots, R_N = positions of the N nuclei

eZ_1, \dots, eZ_N = charge of the N nuclei

M_1, \dots, M_N = masses of the nuclei

r_1, \dots, r_n = positions of the n electrons



Now, our wavefunction is more complicated

$$\Psi(r) \Rightarrow \Psi(R_1, \dots, R_N, r_1, \dots, r_n)$$

* at least, not in any finite amount of time or resource.

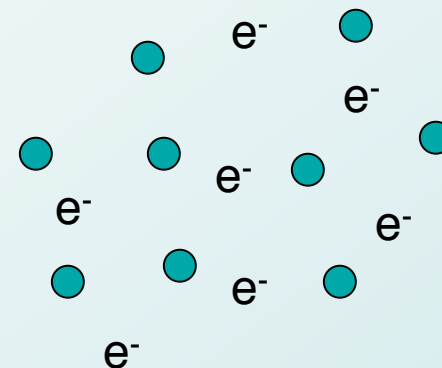
Multi-electron Atoms and Molecules

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eZ_1, \dots, eZ_N = charge of the N nuclei

M_1, \dots, M_N = masses of the nuclei

r_1, \dots, r_n = positions of the n electrons



The Hamiltonian looks like:

$$\hat{H} = \sum_{j=1}^N \left(-\frac{\hbar^2}{2M_j} \right) \nabla_{R_j}^2 + \frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N \frac{Z_i Z_j e^2}{|R_i - R_j|} + \sum_{j=1}^n \left(-\frac{\hbar^2}{2m} \right) \nabla_{r_j}^2 + \frac{1}{2} \sum_{j=1}^n \sum_{i=1}^n \frac{e^2}{|r_i - r_j|} - \sum_{j=1}^N \sum_{i=1}^n \frac{Z_j e^2}{|r_i - R_j|}$$

And our eigenvalue problem looks like:

$$\hat{H}\Psi(R_1, \dots, R_N, r_1, \dots, r_n) = \varepsilon \Psi(R_1, \dots, R_N, r_1, \dots, r_n)$$

In general, we really cannot solve this. We need to make some approximations first. These are related in particular into decoupling the system of interacting particles.

Approximations

- No relativity
 - we have already assumed this, as we are not solving the Dirac equation
- Born-Oppenheimer Approximation
 - the nuclei are stationary with fixed ion positions R
 - i.e., we fix the positions R , and then determine the reduced wavefunction for the electrons
 - By doing this and scanning over all possible configurations R , we can find the global minimum for the energy
 - In reality, we need not scan - we can shift the ions in the directions that further minimize the energy

$$\hat{H}(\{R_i\})\Psi(r_1, \dots, r_n) = \epsilon \Psi(r_1, \dots, r_n)$$

- Single Particle Approximation

$$\Psi(r_1, \dots, r_n) = \Psi_1(r_1)\Psi_2(r_2)\dots\Psi_n(r_n)$$

But: Why would we expect this to work, a priori? How do we choose the Ψ_i 's?

Born-Oppenheimer

A proton is 1836 times heavier than an electron. So, to a good approximation, the electrons can adjust “instantaneously” to changes in the positions of the nuclei.

Thus, the electronic wavefunction depends only on the positions of the nuclei and not on their momenta.

The total energy (as well as wavefunction) can be divided into a nuclear part and an electronic part.

Dynamics simulations are still possible, but for each arrangement of the nuclei the Schrödinger equation is solved for the electrons in the field of the nuclei.

The More General Case

As a simple guess, one may try to write the wavefunction as a product of orbitals:

$$\Psi(1,2,...N) = \varphi_1(1)\varphi_2(2)...\varphi_N(N)$$

This is the Hartree product, and while it's a good start, it is not acceptable.

This is because the wavefunction is not antisymmetric: exchanging pairs of electrons does not give the negative of the wavefunction.

A very important conclusion of the Hartree product description is that the probability of finding an electron at a particular point in space is independent of the probability of finding any other electronic at that point in space.

Thus, the motions of electrons in this description are uncorrelated.

Slater Determinant

The simplest way to fix the antisymmetry issue is to write a wavefunction as a Slater determinant.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_N(N) \end{vmatrix}$$

This formalism guarantees antisymmetry since exchanging any two rows of a determinant leads to a change in sign (and represents the process of exchanging two electrons).

As a nice bonus, the Slater determinant also guarantees that no two electrons can occupy the same orbital (Pauli tells us this) since that corresponds to two rows being identical.

LCAO

In many quantum mechanical calculations, each molecular orbital is expressed as a linear combination of atomic orbitals (the “LCAO” approach).

In this approximation, each molecular orbital is written as a summation:

$$\varphi_i = \sum_{\mu=1}^K c_{\mu i} \phi_{\mu}$$

For example, in an LCAO picture of the H_2 molecule, there are 2 electrons of opposite spin occupying a spatial orbital $\sigma = (1s_A + 1s_B)$.

Calculating the Energy

$$E = \frac{\int \Psi^* H \Psi d\mathbf{r}}{\int \Psi^* \Psi d\mathbf{r}}$$

The energy calculation is as simple as evaluating these integrals...

Ok, well it's not all that simple, but after a bit of math, one can generalize its calculation to a set of 1-electron and 2-electron integrals.

Most integrals are zero, although there still remain a very large number to evaluate.

The Coulomb and “exchange” integrals are usually the most time-consuming.

What's the exchange interaction? Is it classical?

Hartree-Fock

Remember that for a many-body quantum system there is no “correct” picture.

However, we can use a criterion to discern whether one proposed wavefunction is “better” than another.

The variation theorem is one mechanism - it states that the energy calculated from an approximation to the true wavefunction will always be greater than the true energy.

Thus, the better the wavefunction, the lower the energy. At a minimum, the first derivative of the energy will be zero.

The Hartree-Fock simply impose this condition on the expression for the energy, given a form of the wavefunction of the Slater determinant, and also given a constraint that the orbitals remain orthonormal.

Basis Sets

Basis sets are usually composed of atomic functions. Why?

“Slater type” orbitals are exponential in form and are solutions to the radial part of the simple Hydrogen atomic orbital picture.

However, Slater orbitals are never used because it takes too long to evaluate exponentials, and the multi-center integrals are very difficult to solve.

Instead, what is almost exclusively done is to use Gaussian functions, of the form $\exp(-\alpha r^2)$. If α is large, the function does not spread out very far, while if α is small it gives a large spread.

Since the product of two Gaussians can be represented by a third Gaussian, the two-electron integrals become much simpler to evaluate.

One disadvantage, though, is that a Gaussian doesn't look quite like what we want.

