Today's lecture: the structure of atoms, how atoms interact to form molecules, and how molecules interact with each other… all at the "first principles" level, i.e., no empirical constants or experimentally-derived information.

Basics of quantum theory

Neglecting relativistic effects, all matter is described at a fundamental level by quantum theory. The central feature of this theory is the multi-body **wavefunction:**

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, t)$$

Here, $\mathbf{r}_1, \mathbf{r}_2$, …, etc. are the positions of all fundamental particles in the system (electrons, protons, neutrons) and each $\mathbf{r}$ is a vector (x, y, z). The wavefunction evolves in time, t.

The wavefunction takes on complex values, of the form $a + bi$.

The *physical* significance of the wavefunction is that $\Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, t)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, t)$ is proportional to the joint probability that particle one is at $\mathbf{r}_1$, particle 2 is at $\mathbf{r}_2$, etc, all at the time t. Here $*$ denotes the complex conjugate, i.e., $a - bi$. The quantity $\Psi^*\Psi$ therefore is always real and positive, $a^2 + b^2$.

$$\wp(\mathbf{r}_1, \mathbf{r}_2, \ldots; t) \propto \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, t)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, t)$$

For a single particle, such as a single electron, we have:

$$\wp(\mathbf{r}; t) \propto \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)$$

Quantum mechanics determines the wavefunction up to an arbitrary multiplicative constant. Therefore, we can normalize the wavefunction by demanding that the probabilities sum to one when integrated over the entire space of coordinates available to every particle. For a single particle,

$$\wp(\mathbf{r}; t) = \frac{\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)}{\int \Psi^*(\mathbf{r}', t)\Psi(\mathbf{r}', t) d\mathbf{r}'}$$

Sometimes the notation τ is used instead of $\mathbf{r}$ to indicate integration over all space:

$$\wp(\mathbf{r}; t) = \frac{\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)}{\int \Psi^*(\mathbf{r}', t)\Psi(\mathbf{r}', t) d\tau}$$

The wavefunction describes the evolution of *probabilities*. This is very different from Newtonian mechanics, in which each particle has an exact position at time t, and not a distribution of probable positions. Quantum mechanics says that this distribution is the *most* we can possibly know about the system; we cannot predict the position of the particles to more accuracy. There is some inherent randomness in nature, and the best we can do is predict the probabilities of different possible outcomes.

This may sound a bit strange, because we are not used to this kind of behavior at the macroscopic scale. Indeed, for large objects, these probability distributions are very narrowly peaked relative to the object size, such that we can usually say, from a macroscopic scale of measurement, exactly where an object lies in space. For small objects, like atoms and electrons, these distributions become significant.

The wavefunction is determined by the **Schrodinger equation**, the quantum-mechanical analogy of Newton's equations of motion. For a single particle traveling in a potential energy field, Schrodinger's equation reads:

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

$\hbar = h/2\pi$ where h is Planck's constant, a fundamental constant that, in a very loose sense, governs the scale of quantum randomness. Classical deterministic behavior (i.e., Newton's equations) are recovered in the limit $h \to 0$.

m is the mass of the particle.

∇^2 is the Laplacian operator, which in Cartesian coordinates is given by $\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$.

$V(\mathbf{r})$ is the potential energy function, or just the "potential", which returns the potential energy of the particle as a function of its position within the field

Note that the Schrodinger equation is a differential equation that is first order in time and second order in position. To solve it, we can use the separation of variables technique, where we write the wave function as the product of a spatially-dependent function and a time-dependent function: $\Psi(\mathbf{r},t)=\psi(\mathbf{r})T(t)$. Making this substitution, we have,

$$-\frac{\hbar^2}{2m}T(t)\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\psi(\mathbf{r})T(t)=i\hbar\psi(\mathbf{r})\frac{\partial T(t)}{\partial t}$$

Rearranging so that all the spatial terms are on the left and the time-dependent terms on the right, we get

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(\mathbf{r})}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r}) = i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t}$$

The only way this equation can be satisfied is if both sides equal the same time- and position-independent constant. Let this constant be E. It turns out that the constant is a possible energy of the particle, which is the reason for our choice of notation. Setting the LHS of this equation equal to the constant, and doing some slight rearrangement, yields

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

This particular equation is called the **time-independent Schrodinger equation.** It gives the part of the Schrodinger equation that depends only on position. It is common to rewrite the left hand side as an operator called the **Hamiltonian**, H, such that

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad \text{where} \quad H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

An **operator** is simply a mapping of one function to another function. Quantum mechanics makes extensive use of operators, as all observables (like energy, momentum, velocity, etc) are formulated as operators.

The expectation (average observed) value of any operator A is given by an expression of the form:

$$\frac{\int \psi^* A\psi d\tau}{\int \psi^*\psi d\tau}$$

For example, the expected energy for an arbitrary wavefunction ψ and given Hamiltonian H is found by:

$$E = \frac{\int \psi^* H\psi d\tau}{\int \psi^*\psi d\tau}$$

The potential energy operator is:

$$U = \frac{\int \psi^* V\psi d\tau}{\int \psi^*\psi d\tau}$$

The kinetic energy operator is:

$$K = \frac{\int \psi^* \left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi d\tau}{\int \psi^*\psi d\tau}$$

Eigenfunctions and eigenvalues

The Hamiltonian operator, when applied to the wavefunction, returns the energy times the wavefunction. This is a kind of eigenvalue problem: an operator applied to a function yields a number times that same function.

Such problems give rise to a discrete set of solutions: a set of eigenfunctions possible for ψ and eigenvalues possible for E, but not a continuous range of values. In other words, for a given potential field V and hence a specific Hamiltonian H, the energy of the particle can only take on certain, discrete values.

This is an important, physical aspect of quantum mechanics: energies are discretized. A particle cannot have any energy, as in Newtonian physics. Instead, it must have one from the list of energy eigenvalues. In fact, the observation of discrete energetics in the study of hydrogen spectroscopy was one of the initial motivations that led Schrodinger to discover this equation.

The solutions ψ and E to the Schrodinger equation form an infinite family of eigenfunctions and eigenvalues, respectively. We can notate them with the subscript n:

$$H\psi_n = E_n\psi_n$$

Importantly, the eigenfunctions form an **orthonormal** basis set. That is, any arbitrary wavefunction can be expressed as a linear combination of these. Assuming the ψ_n are all normalized, an arbitrary wavefunction ψ can be written as:

$$\psi = \sum_n c_n\psi_n$$

where the c_n are coefficients given by:

$$c_n = \int \psi_n^*\psi d\tau$$

This is analogous to vector mathematics: any three-dimensional vector can be expressed as a linear sum of unit vectors along the x, y, and z axes. The coefficients in the linear sums are given by dot products.

Because the eigenfunctions are orthonormal, the following identity holds:

$$\int \psi_n^*\psi_m d\tau = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

Electronic structure and the Born-Oppenheimer approximation

We would like to use the Schrodinger equation to compute the **electronic structure** of arbitrary atoms and molecules. By electronic structure, we mean the wave function for all of the electrons in the system, for a fixed set of nuclear coordinates. In other words, we place the nuclei at fixed locations in space and solve the time-independent Schrodinger equation for all of the electrons interacting with them.

The electronic structure provides the energies associated with the electron-electron and electron-proton interactions. Electrons can exist in any number of excited states, which correspond to different eigenfunctions of the wavefunction, but typically we are interested in the one with the lowest energy, the so-called **ground-state** of the system.

In principle, a molecule is determined by a complete wavefunction that includes both electron and nuclear (protons, neutrons) degrees of freedom. However, the masses of nuclei are much greater than that of electrons. As a result, we can think of the electrons as much faster degrees of freedom that adjust rapidly to changes in the positions of the nuclei. Mathematically, we can write the total wavefunction as a product of nuclear and electronic wavefunctions. This is the so-called **Born-Oppenheimer approximation**:

$$\Psi_{\text{tot}}(\text{nuclei,electrons}) = \Psi(\text{nuclei})\Psi(\text{electrons})$$

A consequence of this approximation is that the total energy of the system is a sum of the nuclear energy (electrostatic repulsion of positively charged nuclei) with the electronic energy (electrons with each other and with the nucleus):

$$E_{\text{tot}} = E_{\text{nuc}}(\text{nuclei-nuclei}) + E(\text{electrons-nuclei and electrons-electrons})$$

We will use E hereon to describe the electronic energy alone.

The basic idea of electronic structure calculations is to map out the **ground state energy surface**, that is, the ground state electronic energy as a function of the positions of the nuclei. This involves several steps:

1. For a fixed set of nuclear coordinates $\mathbf{R}$, solve the time-independent Schrodinger equation for the electrons to obtain the eigenfunctions $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$, where $\mathbf{r}_i$ denote the electron positional degrees of freedom.

2. Compute the ground-state energy E_0 from the lowest-energy wavefunction.

3. Change to a new set of nuclear coordinates and repeat.

The hydrogen atom

The hydrogen atom is the only neutral atomic system for which the electronic structure can be found exactly (analytically). This is a classic problem in quantum mechanics.

The Hamiltonian for one electron orbiting one proton is:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

Here, the last term is the Coulomb potential energy of an electron orbiting a proton at the origin, and r is its radial distance from it. e is the electron charge and ϵ_0 is the permittivity of free space.

The wave function can be solved by a transformation of the electron position to spherical coordinates and the use of the separation of variables technique. The final solution is of the form:

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi)$$

Here, there is a radial part given by $R_{nl}(r)$ and an angular part given by $Y_{lm}(\theta,\phi)$. The equation describes an infinite family of functions (the eigenfunctions) that all satisfy Schrodinger's equation for the hydrogen atom. We refer to these different wavefunction solutions as **orbitals**.

The integers n, l, m are quantum numbers and have the following ranges:

- $n = 1,2,3,\ldots$ is the principal quantum number. Gives the shell of the electron.
- $l = 0,1,\ldots,(n-1)$ is the azimuthal quantum number. Gives the type of orbital, $0 = s, 1 = p, 2 = d, 3 = f$
- $m = -l, -l+1, \ldots, 0, \ldots, l-1, l$ is the magnetic quantum number.

The energy eigenvalue associated with an eigenfunction is dependent only on the principal quantum number n:

$$E = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \qquad \text{with } \mu = \frac{m_p m_e}{m_p + m_e}$$

The functions R_n contain so-called Laguerre polynomials. The first few are given by:

$$R_{10}(r) = 2\zeta^{\frac{3}{2}}\exp(-\zeta r)$$

$$R_{20}(r) = 2\zeta^{\frac{3}{2}}(1-\zeta r)\exp(-\zeta r)$$

$$R_{21}(r) = \left(\frac{4}{3}\right)^{\frac{1}{2}}\zeta^{\frac{5}{2}} r\exp(-\zeta r)$$

Here, $\zeta \equiv 4\pi^2 m_e e^2/h^2 n$.

The functions Y_{lm} are the so-called spherical harmonics. The first few are:

$$Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_{1-1}(\theta,\phi) = -\left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta\, e^{i\phi}$$

$$Y_{10}(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta\, e^{-i\phi}$$

$$Y_{11}(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta$$

In any case, these functions are known analytically and thus the full spectrum of wavefunction eigenfunctions is known.

Polyelectronic systems

For multi-electron systems, it is impossible to solve the Schrodinger equation exactly. There are several challenges here:

- the three-body problem – no solutions can be found for more than two interacting particles
- electron spin – electron orbitals can either have up or down spin, labeled as α and β. Each *spatial* orbital ψ can accommodate up to two spins. We must account for this fact in our solutions.
- indistinguishability – the wavefunction must change sign upon swapping the identities of two electrons because they are indistinguishable fermions.

The combination of a spatial wavefunction orbital with a spin wavefunction is called a *spin orbital* and notated by the symbol χ.

$$\chi_{nlms} = \psi_{nlm} s \quad \text{where } s = \alpha \text{ or } \beta$$

For any arbitrary atom or molecule with M nucleii and N electrons, the Hamiltonian can be written as

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 \; - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k}{R_{ik}} + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

Here, the first term again corresponds to the kinetic energy operator. The middle term gives the Coulombic interaction of electrons with nuclei, where Z_k is the charge unit of nucleus k. The final term is a pairwise sum over electrons that accounts for electronic repulsion.

Variational theory

Though we cannot solve for the wavefunction exactly given the polyelectronic Hamiltonian, a remarkable theorem allows us to find approximations to it. This variational theorem says that the expectation value for the energy of any trial wavefunction will give an energy greater than or equal to the ground-state energy of the true solution to Schrodinger's equations. Thus, we can find approximate solutions to Schrodinger's equation by minimizing the expectation energy with respect to a trial solution.

The proof of the variational theorem is actually quite simple. Consider an arbitrary trial wavefunction written as a sum over orthornormal basis functions that are true solutions for the Hamiltonian of interest:

$$\psi = \sum_i c_i \psi_i$$

To find the expectation value of the energy E for the trial wave function,

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$$

Substituting the expression above,

$$\begin{aligned} E &= \frac{\sum_i \sum_j c_i c_j \int \psi_i^* H \psi_j d\tau}{\sum_i \sum_j c_i c_j \int \psi_i^* \psi_j d\tau} \\ &= \frac{\sum_i \sum_j c_i c_j \int \psi_i^* E_j \psi_j d\tau}{\sum_i \sum_j c_i c_j \int \psi_i^* \psi_j d\tau} \\ &= \frac{\sum_i \sum_j c_i c_j E_j \int \psi_i^* \psi_j d\tau}{\sum_i \sum_j c_i c_j \int \psi_i^* \psi_j d\tau} \end{aligned}$$

Using the orthonormality condition, the integrals vanish for all but $i = j$,

$$E = \frac{\sum_i c_i^2 E_i}{\sum_i c_i^2}$$

Subtracting the ground-state energy E_0 from both sides,

$$E - E_0 = \frac{\sum_i c_i^2 (E_i - E_0)}{\sum_i c_i^2}$$

By the definition of E_0, $E_i - E_0 \geq 0$ on the RHS, since E_0 is the lowest value of the E_i. Therefore, the RHS is always zero or positive and we must have

$$E \geq E_0$$

The idea of the variational principle is therefore the following:

> Pick an approximate form of the wavefunction for the polyatomic system. Then, find the optimal such form by minimizing the expectation energy with the true Hamiltonian with respect to any free parameters. Lower expectation energies indicate better solutions.

Hartree-Fock approach and Slater determinants

The Hartree-Fock approach posits a trial form of the N-electron wavefunction and uses the variational theorem to obtain an approximate solution. The basic idea here is to express the wavefunction as a product of individual spin orbital solutions, the so-called **Hartree product:**

$$\psi(1,2,3,\dots,N) = \chi_1(1)\chi_2(2)\dots\chi_N(N)$$

Here, the numbers written are abbreviations to the electron degrees of freedom. Unfortunately, this form of the trial wavefunction does not obey the indistinguishability requirement for fermions, that the swapping of two particles generates an identical but negated wavefunction:

$$\chi_1(1)\chi_2(2)\dots\chi_N(N) \neq -\chi_1(2)\chi_2(1)\dots\chi_N(N)$$

since in general all of the χ functions can be different.

Instead of the Hartree product, we want to use a similar multiplicative combination of individual spin orbitals, but ones that form the negative upon swapping. For two electrons, we could make the choice,

$$\psi(1,2) = \frac{1}{\sqrt{2}}[\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)]$$

Notice that swapping 1 and 2 returns the negative wavefunction and thus satisfies the indistinguishability criterion:

$$\frac{1}{\sqrt{2}}[\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)] = -\frac{1}{\sqrt{2}}[\chi_1(2)\chi_2(1) - \chi_1(1)\chi_2(2)]$$

The square root stems from the normalization condition.

For an arbitrary number of electrons, forming combinations of orbitals such as this can be achieved using the determinant of a matrix, the so-called **Slater determinant**:

$$\psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

The determinant is a natural way to achieve the indistinguishability principle: swapping two rows or two columns causes the determinant to change sign, exactly what we need for our trial wavefunction. Moreover, if two rows or columns are identical, the determinant would be zero. Physically, this would mean that two electrons were occupying the same orbital and same spin, forbidden by the Pauli exclusion principle.

The Hartree-Fock approximation to the wavefunction is equivalent to a mean-field solution of Schrodinger's equation in which each electron moves within an average field due to the presence of all of the other electrons.

We will now consider only closed-shell systems, i.e., systems in which all electrons appear in pairs. There are special methods for treating open-shell systems, but we will not cover these. Substituting the Slater determinant as a trial wavefunction into the polyelectronic Hamiltonian gives the following expression for the expectation energy, after simplification of integrals:

$$E = 2\sum_{i=1}^{N/2} H_{ii}^{\text{core}} + \sum_{i=1}^{N/2}\sum_{j=1}^{N/2} 2\big(J_{ij} - K_{ij}\big)$$

H_{ii}^{core} gives the kinetic and potential energy of the electrons moving in the field of the nuclei:

$$H_{ii}^{\text{core}} = \int d\tau_1 \chi_i(1)\left[-\frac{1}{2}\nabla_{\text{i}}^2 - \sum_{k=1}^{M}\frac{Z_k}{R_{1k}}\right]\chi_i(1)$$

J_{ij} gives the electrostatic repulsion between electrons:

$$J_{ij} = \int d\tau_1 d\tau_2 \chi_i(1)\chi_j(2)\left[\frac{1}{r_{12}}\right]\chi_i(1)\chi_j(2)$$

K_{ij} gives the so-called **exchange** interaction. This stems from the tendency of electrons with the same spin to "avoid" each other, per the Pauli exclusion principle:

$$K_{ij} = \int d\tau_1 d\tau_2 \chi_i(1)\chi_j(2)\left[\frac{1}{r_{12}}\right]\chi_i(2)\chi_j(1)$$

Notice that the only difference here is the swapping of identities in the second set of orbitals. All equations here have been written in atomic units, and fundamental constants have been omitted for clarity.

Linear combination of atomic orbitals (LCAO)

Now that we can use the Slater determinant to find solutions that obey the indistinguishability principle, we need to specify forms for the functions χ_i that go into them. The easiest solution here is to use the analytic basis functions that we determined for the hydrogen atom. We can express each χ_i as a sum of these functions, with coefficients:

$$\chi_i = \left[\sum_{\nu=1}^{K} c_{\nu i}\phi_\nu\right] s_i$$

Here, the ϕ_ν are the solutions to the wavefunction eigenfunction expansion for the hydrogen atom. The s_i give the spins. The c_{ij} are coefficients that will be determined (optimized) by variational minimization of the expectation energy:

$$\frac{\partial E}{\partial c_{\nu i}} = 0$$

It is important that the minimization is constrained so that the orbitals χ_i are orthonormal to each other. This is accomplished using Lagrange multipliers.

Using the expression above for the orbital energy, this minimization can be performed. Assume we use K basis functions in our expression for χ_i. The result gives the **Roothaan-Hall equations** and has the form of a set of matrix equations:

$$\mathbf{FC} = \mathbf{SCE}$$

$\mathbf{F}$ is the Fock matrix; its elements are given by,

$$F_{\mu\nu} = \int d\mu_1 \phi_\mu(1) \left[-\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{R_{1k}} \right] \phi_\nu(1) - \sum_{j=1}^{N/2} \sum_{\lambda=1}^{K} \sum_{\sigma=1}^{K} \left[2 \int d\nu_1 d\nu_2 \phi_\mu(1)\phi_\nu(2) \left(\frac{1}{r_{12}}\right) \phi_\lambda(2)\phi_\sigma(2) - \int d\nu_1 d\nu_2 \phi_\mu(1)\phi_\lambda(2) \left(\frac{1}{r_{12}}\right) \phi_\nu(2)\phi_\sigma(2) \right]$$

The matrix $\mathbf{C}$ contains the coefficients to be determined

$$C_{\nu i} = c_{\nu i}$$

The matrix $\mathbf{S}$ gives the overlap between the orbitals:

$$S_{ij} = \int \chi_i \chi_j d\tau$$

Finally, $\mathbf{E}$ gives the orbital energies for the K optimal orbitals that are determined:

$$\mathbf{E} = \begin{pmatrix} \epsilon_1 & 0 & \cdots & 0 \\ 0 & \epsilon_2 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \epsilon_K \end{pmatrix}$$

The Roothan-Hall equations are matrix equations that can be solved using matrix algebra to give back the optimal coefficients and orbital energies. However, these equations must be solved iteratively because elements of both $\mathbf{F}$ and $\mathbf{S}$ depend on the coefficients themselves. The Roothan-Hall procedure iteratively operates in this way. We won't go into details here.

The minimum number of basis orbitals that can be used K is equal to the number of electrons, N. More will allow the treatment of unoccupied energy levels and can enhance the accuracy of the calculations. Often, however, one can reach the **Hartree-Fock** limit where the energy no longer decreases with the addition of more basis functions.

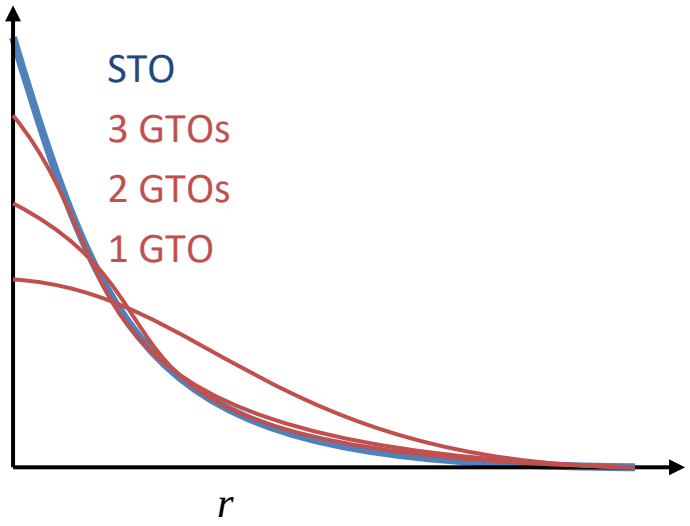
Basis sets

Most of the time spent solving the Roothan-Hall equations numerically is devoted to computing the integrals in the Fock and overlap matrices. Typically so-called **Slater-type orbitals (STOs)** are used in the basis functions ϕ_ν, which are inspired by the form of the solutions for the hydrogen atom to first order in the Laguerre polynomials:

$$R_n(r) = (2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}} r^{n-1} \exp(-\zeta r)$$

Unfortunately this functional form for the orbitals, while physically inspired, results in computational challenges. What makes the use of STOs challenging is that the integrals involving orbitals sitting on different nuclei can be very difficult to compute.

A simple solution has been to approximate STOs with Gaussian functions instead—so-called **Gaussian type orbitals (GTOs)**. That is, one uses multiple Gaussians to approximate the form of the STOs. The advantage of Gaussians is that the product of two Gaussians centered at two different locations is another Gaussian (and can computed analytically) such that the orbital integrals can be computed very fast.



A special notation describes the basis sets used in common ab initio calculations.

- STO-3G – a *minimal* basis set in which three Gaussians are used to represent each Slater-type orbital. Useful for quickly computing molecular geometries, but not very accurate.
- 3-21G – three Gaussians are used for the core orbitals. For the valence electrons, a *split* basis set is employed where two Gaussians are used for a contracted part of the wavefunction and one for the diffuse part. This is important for atoms like oxygen and fluorine where the minimal basis sets don't allow for the valence orbitals to expand or contract in response to the molecular environment.
- 6-31G – the same as above but with six Gaussians for the core orbitals; more accurate.
- 6-31G* – the same as above but allowing polarization (i.e., distortion) of non-hydrogen orbitals to accommodate asymmetry. This basis set might be considered a standard high accuracy calculation, although it is expensive.

Often, one wants to find an optimal molecular geometry for a molecule. This involves searching nuclear configurations for the one with lowest energy, and thus requires a complete electronic structure determination upon each change of nuclear coordinates. Typically fast, approximate basis sets like STO-3G are first used in this geometry optimization. Then, when the geometry is near the energy minimum, more accurate and expensive basis sets like 6-31G* are employed to refine the calculations.

Computing the electron density

One of the most important properties we can examine from an electron structure calculation is the **electron density**, that is, the probability density with which we expect to see an electron as a function of spatial position. The electron density gives important properties of a molecule, such as the dipole, and is the starting point for developing simpler, fixed-charge models of molecules that we will discuss in a later lecture.

For a set of N orthonormal one-electron orbitals ψ_i, we can use the probabilistic interpretation of the wavefunction to develop an expression for the electron density:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

Notice that we have

$$N = \int \rho(\mathbf{r}) d\mathbf{r}$$

If the orbitals are expressed as a sum of K basis functions ϕ_ν, as in the Rootham-Hall approach, we can rewrite the electron density as

$$\rho(\mathbf{r}) = \sum_{\mu=1}^{K} \sum_{\nu=1}^{K} \left(\sum_{i=1}^{N} c_{\mu i} c_{\nu i} \right) \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r})$$

Summary of Hartree-Fock

The basic conceptual approach to these computations is the following:

Approximate:

$$\psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

Expand each spin orbital in terms of K ($\geq N$) hydrogen-like basis solutions ϕ_ν:

$$\chi_i = \left[\sum_{\nu=1}^{K} c_{\nu i}\phi_\nu\right] s_i$$

Model each ϕ_ν using a weighted finite sum of Gaussian-type orbitals (GTOs):

$$\phi_\nu = \sum a_i \frac{1}{\sigma_i\sqrt{2\pi}} e^{-\frac{|\mathbf{r}-\bar{\mathbf{r}}_i|^2}{2\sigma_i^2}}$$

Here, the a_i are chosen to reproduce the corresponding Slater-type orbitals (STOs).

To solve for the wavefunction, one finds the optimal coefficients $c_{\nu i}$ in its basis expansion. There are $K \times N$ of these. Use the variational principle:

$$\frac{\partial E}{\partial c_{\nu i}} = 0$$

subject to the constraint that the χ_i are orthonormal to each other. Here,

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$$

where ψ is the wavefunction defined above, and the Hamiltonian operator is:

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{N}\sum_{k=1}^{M}\frac{Z_k}{R_{ik}} + \frac{e^2}{4\pi\epsilon_0}\sum_{i<j}^{N}\frac{1}{r_{ij}}$$

Finally, compute the electron density using the optimal coefficients:

$$\rho(\mathbf{r}) = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K}\left(\sum_{i=1}^{N} c_{\mu i}c_{\nu i}\right)\phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r})$$

Density functional theory

A complementary approach to Hartree-Fock theory for determining electronic structure is the **density functional theory** (DFT) of Hohenberg, Kohn, and Sham. This theory is now standard in ab initio modeling. Instead of computing the multielectron, multidimensional wavefunction, density functional theory is concerned with computing the electron density $\rho(\mathbf{r})$.

DFT is enabled by a remarkable theorem due to Hohenberg and Kohn (1964) that shows that the ground state wavefunction and energy of a polyelectronic system is uniquely determined by a functional of the electron density. In mathematical terms,

$$E_0[\rho(\mathbf{r})]$$

Here, the brackets indicate the presence of a *functional.* A functional is a mathematical operation that depends on the entire behavior of a function, not just its value at a specific point. For example, the functional:

$$F[y] = \int_0^1 y(x)dx$$

depends on the complete behavior of the function y between $x = 0$ to 1. Functionals differ from functions in that a function takes a single value as an argument, whereas a functional takes a function itself.

In DFT, the ground state energy functional is written as (Kohn and Sham, 1965):

$$E[\rho(\mathbf{r})] = \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{KE}[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

The first tem on the RHS gives the interaction of the electrons with external potentials; here, this is their interactions with the nuclei:

$$\int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = -\int \sum_{k=1}^{M} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r}$$

The second term gives the kinetic energy. It is assumed to be identical to that which would be attained for an equivalent system of *noninteracting* electrons:

$$E_{KE}[\rho(\mathbf{r})] = \sum_{i=1}^{N} \int \psi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2}\right) \psi_i(\mathbf{r})\, d\mathbf{r}$$

The third term, the Hartree term, is given by the electron-electron repulsive interactions:

$$E_H[\rho(\mathbf{r})] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

The exchange-correlation functional is not known exactly, but it is a *universal* function, independent of the specific system at hand. It includes exchange and correlation effects, as well as the difference between the true kinetic energy and the noninteracting kinetic energy assumption

defined above. A number of approximations exist for E_{XC}. The simplest is the so-called **local density approximation** (LDA), given by:

$$E_{XC}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\epsilon_{XC}(\rho(\mathbf{r}))d\mathbf{r}$$

The LDA simply states that the only the local electron density affects the exchange-correlational energy, and that it can be approximated by the use of a simple function of ρ. Here, $\epsilon_{XC}(\rho)$ is typically taken from simulations of homogeneous electron gas. These are sometimes fitted to simple forms. As one example, Gunnarsson and Lundqvist proposed (1976):

$$\epsilon_{XC}(\rho) = -\frac{0.458}{r_s} - \frac{0.0666}{2}\left[(1+x)\log(1+x^{-1}) - x^2 + \frac{x}{2} - \frac{1}{3}\right]\left(\frac{r_s}{11.4}\right) \;\; ; \;\; \frac{4\pi}{3}r_s^3 = \rho^{-1}$$

Minimizing the electron density functional

To solve for $\rho(\mathbf{r})$ using the functional energy above, one uses the variational principle to minimize E. This is actually a *functional* minimization since we are finding an entire function, rather than a single number or set of numbers, that minimizes the expression of interest:

$$\frac{\delta}{\delta\rho(\mathbf{r})}\left[E[\rho(\mathbf{r})] - \mu\int \rho(\mathbf{r})d\mathbf{r}\right] = 0$$

Here, μ is a Lagrange multiplier that ensures that:

$$\int \rho(\mathbf{r})d\mathbf{r}$$

is constant, and equal to N, the total number of electrons.

To solve this functional minimization, we introduce an expression for the electron density in terms of N orbital equations:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2$$

Evaluating the functional minimization with this expression for the density leads to the Kohn-Sham equation:

$$\left\{-\frac{\nabla_1^2}{2} - \left(\sum_{k=1}^{M}\frac{Z_k}{|\mathbf{r}_1 - \mathbf{R}_k|}\right) + \int\frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_2 + \frac{\delta E_{XC}[\rho(\mathbf{r}_1)]}{\delta\rho(\mathbf{r}_1)}\right\}\psi_i(\mathbf{r}_1) = \epsilon_i\psi_i(\mathbf{r}_1)$$

This equation must be solved self-consistently:

1. An initial approximation for $\rho(\mathbf{r})$ is guessed.
2. The Kohn-Sham equation is used to derive a set of orbitals ψ_i and orbital energies ϵ_i. This approach is very similar to the Hartree-Fock method, where the orbitals are expressed as a linear sum of basis functions with coefficients that are determined variationally.
3. The derived orbitals are used to update the electron density via the equation above.
4. The process is iterated at step 2 until the density converges.

Car-Parinello ab initio molecular dynamics

So far, we have only seen electronic structure calculations for fixed positions of atomic nuclei. Often, we would like to be able to examine the time-evolution of the nuclei as well, in order to examine molecular processes. The immediate challenge with this approach is computational expense: every time we move the positions of the nuclei, we require a completely new electronic structure calculation.

Car and Parinello (1985) developed an elegant solution to coupling the time-propagation of moving nuclei with the electronic structure determination. This is often called **ab initio molecular dynamics**. Their approach sets up "equations of motion" for the solutions of the coefficients that approximately follow the variational-minimum orbital coefficients one would find from a DFT solution of the electronic structure at each step. These coefficients are evolved in time as the nuclear positions are evolved. By correctly picking fictitious coefficient "masses" this approach is able to quite accurately reproduce the time evolution of the electronic structure alongside the time-evolution of the nuclear positions.

Limitations and computational expense

Ab initio calculations are computational very expensive. Typically, they can only handle 10^2-10^3 atoms and, if Car-Parinello dynamics is used, time scales on the order of 100ps. One problem with these methods is that the computational expense scales roughly as N^4 where N is the number of basis functions (which must at least be the electrons). This arises due to the fact that the integrals over two-body interactions involve four spin orbitals, each of which is an expansion in at least N basis functions (Slater type orbitals). This can make ab initio studies prohibitive for even small molecular systems.

Semi-empirical methods

A number of approximate methods have been developed that achieve better performance and scaling than the Hartree-Fock and DFT approaches. These so-called **semi-empirical** methods only

treat the valence electrons explicitly and incorporate parameters fitted to experimental data to make up for this lack of explicit detail in all of the electrons. These methods can treat $\sim 10^3$ atoms and time scales up to 10 ns. The trade-off, however, is that large parameter sets are required from experimental input.