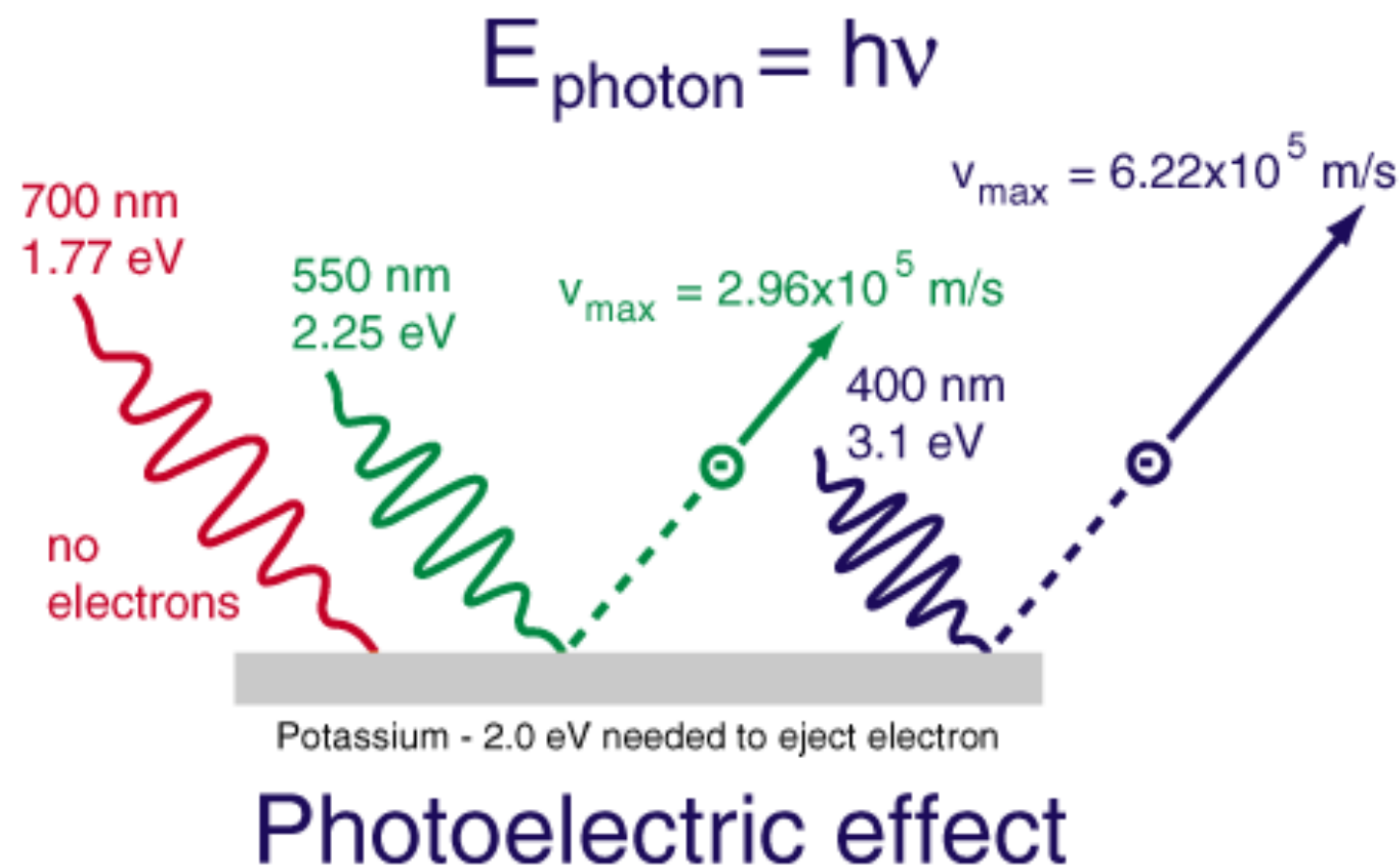


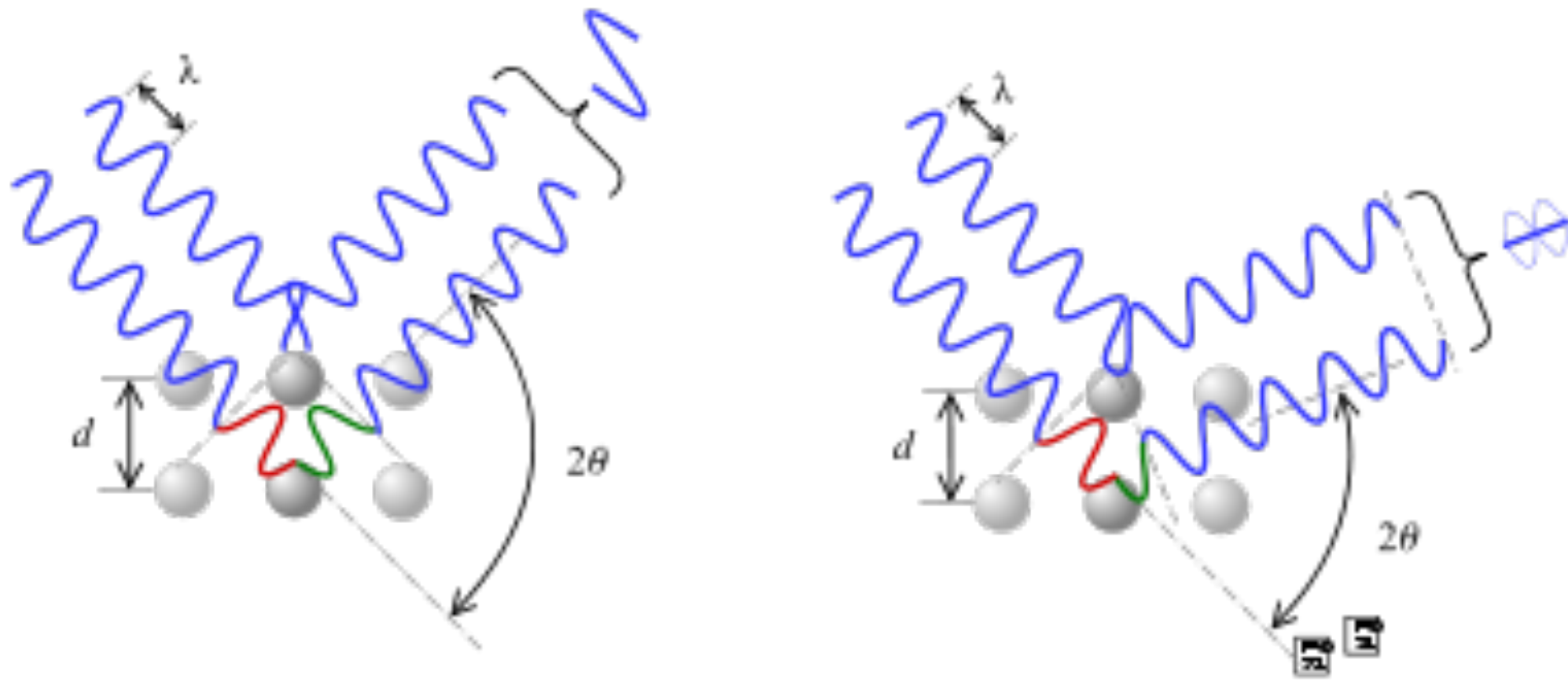
Why quantum mechanics? Several key experiments motivate it

- Photoelectric effect
- Blackbody radiation
- Electron diffraction
- Absorption and emission spectra

Photoelectric effect and absorption and emission spectra are explained by photons



Electron diffraction is explained by the wave properties of particles



The Schrödinger equation describes quantum systems

For a single particle in a potential V :
$$\left[\frac{\hbar^2}{2m} \nabla^2 + V \right] \Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$

$$\nabla^2 \Psi(\mathbf{r}, t) = \nabla \cdot \nabla \Psi(\mathbf{r}, t)$$

$$\nabla^2 \Psi(\mathbf{r}, t) = \frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial x^2} + \frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial y^2} + \frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial z^2}$$

where V is the potential, m the mass, and constants include:

$$i = \sqrt{-1}$$

$$\hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-34} \text{ m}^2 \text{ kg/s}$$

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$$\mathcal{H} \equiv \left[\frac{\hbar^2}{2m} \nabla^2 + V \right]$$

Kinetic energy



Potential energy



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$$\mathcal{H} \equiv \left[\frac{\hbar^2}{2m} \nabla^2 + V \right]$$

If the potential is time-independent: $\mathcal{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$

The wavefunction is normalized; the probability of a state is: $|\Psi(\mathbf{r}, t)|^2$

States are specified
completely by the wavefunction

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The expectation value of any operator is given by: $\langle \hat{A} \rangle = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau}$

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Eigenfunctions form an orthonormal basis set; all other wavefunctions can be expressed in terms of these: $\Psi = \sum_n c_n \Psi_n$

Only a few problems can be solved analytically

- Particle in a box
- Harmonic oscillator
- Hydrogen atom

- Common element: Energy levels are “quantized”

The hydrogen atom (and one electron atoms) can be solved analytically

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

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

n, l, m are quantum numbers:

- $n = 1, 2, 3, \dots$: Shell of electron
- $l = 0, 1, \dots (n-1)$: Type of orbital ($0 = s, 1 = p, 2 = d, 3 = f$)
- $m = -l, -l+1, \dots, 0, \dots, l$

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

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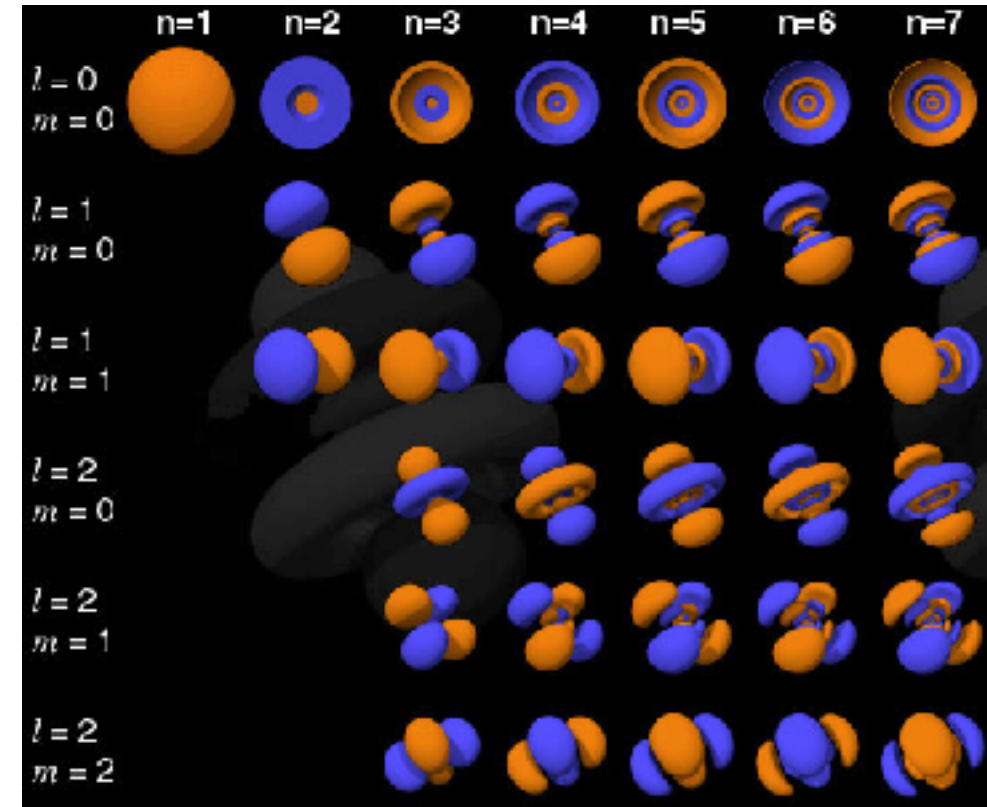
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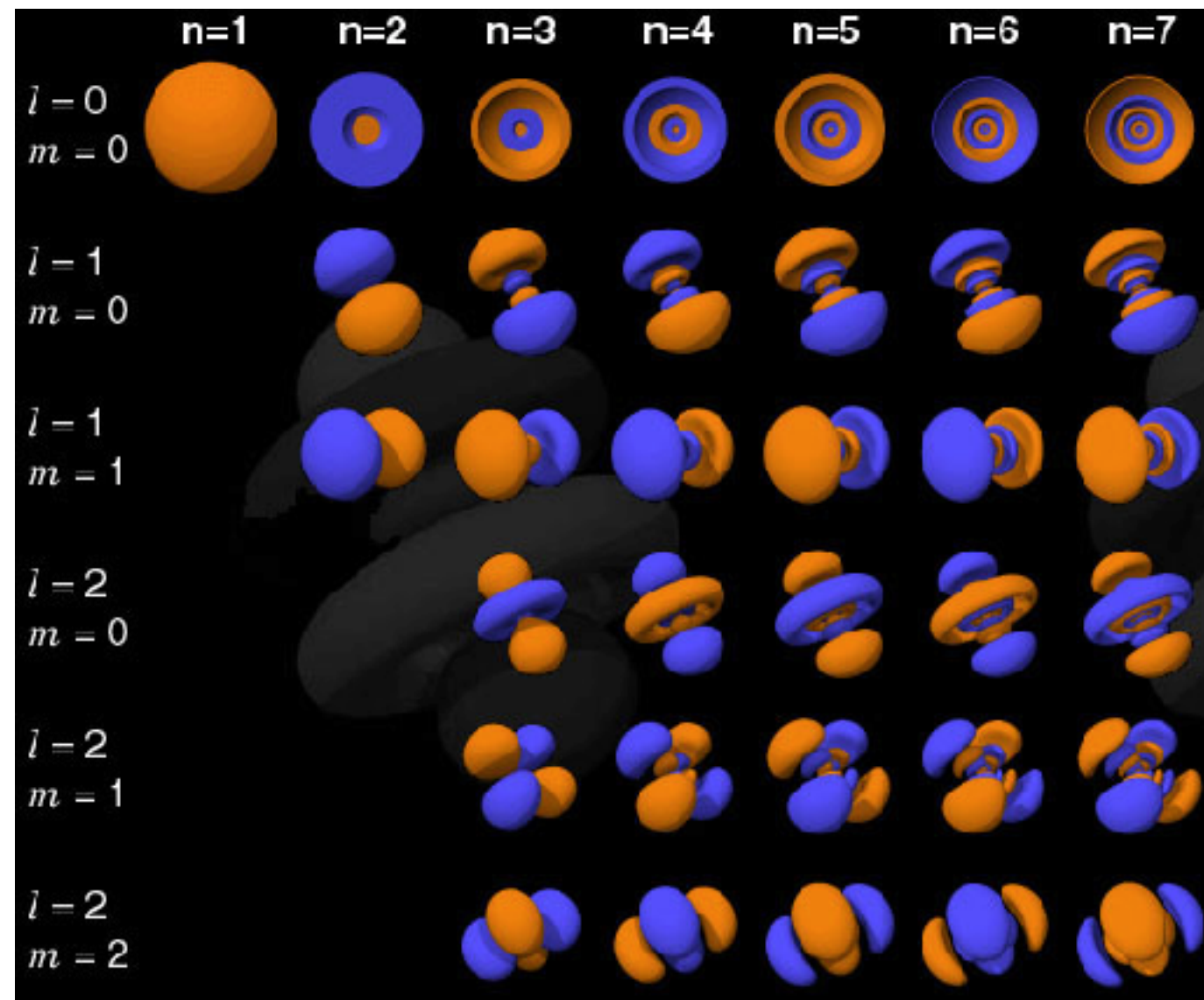


<http://chemistry.beloit.edu/Stars/images/orbitals.jpg>

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The Born-Oppenheimer approximation is for systems with multiple nuclei

- In principle, motion of electrons is coupled to motion of nuclei
 - But electrons are faster
 - Born-Oppenheimer: Assume electrons respond instantaneously, and then take:
$$\Psi_{tot}(nuc, elec) = \Psi(elec)\Psi(nuc)$$
 - Practically: Fix nuclear positions, solve for wavefunctions
- $E_{tot} = E_{nuc}(nuc, nuc) + E(elec-nuc \text{ and } elec-elec)$
 - When we talk about energy, we will be referring to $E(elec-nuc \text{ and } elec-elec)$
 - Now we solve electronic wavefunction for specific nuclear configurations

Polyelectronic atoms present challenges

- *Three-body problem*: No analytical solutions for three or more interacting particles
 - Approximate solutions are possible; can have various forms
- *Electron spin*: When dealing with multiple electrons, we must account for spin
 - No two electrons can have the same quantum state and spin (so only two electrons per quantum state)
- *Indistinguishability*: Electrons are indistinguishable and the wavefunction must change sign on swapping any two electrons

Generally:
$$\mathcal{H} = \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{j=1}^M \frac{Z_j}{R_{ij}} + \frac{e^2}{4\pi\epsilon_0} \sum_{i,j>i}^N \frac{1}{r_{ij}}$$

No analytical solution past hydrogenic atoms

Variational theory enables approximate solutions and simple tests

- Any trial wavefunction will give an energy greater than or equal to the ground state energy of the true solution
 - Can thus find approximate solutions by finding the trial solution that minimizes the energy.
 - Provides upper bound on energies

The variational principle allows for “guessing” of solutions

Guess a functional form

Adjust parameters to minimize the energy

The lowest energy solution is the closest to the true solution

$$\Psi = \sum_i c_n \phi_n, \text{ adjusting the } c_n \text{ to minimize the energy}$$

Hartree-Fock: Come up with a simple functional form for the wavefunction and use the variational theorem

- Express the wavefunction as a product of single-electron wavefunctions
- Use hydrogen orbitals (or something like that) as a starting point
- Use the variational theorem to minimize energy, optimize solution

Hartree-Fock uses the variational theorem with a particular trial wavefunction to obtain an approximate solution

- We do need to track electron spin in addition to spatial wavefunction
 - Denote spin by α, β
 - Wavefunction now $\chi_{nlms} = \psi_{nlm}s$, where s is α or β
- Idea: Write solution for N electrons as product of individual spin orbital solutions (Hartree product):

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

- Doesn't meet exchange criteria, where swapping two particles changes the sign:

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

Slater determinants provide a way to get antisymmetric wavefunctions

- How do we get antisymmetric wavefunction?

- For two particles, could do this: $\psi(1, 2) = \frac{1}{\sqrt{2}} [\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)]$
- Note that now $\frac{1}{\sqrt{2}} [\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)] = -\frac{1}{\sqrt{2}} [\chi_1(2)\chi_2(1) - \chi_1(1)\chi_2(2)]$

- An easy way to accomplish this generally is with a Slater determinant:

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

- Changes sign if we swap any two rows/columns
- Zero if two rows or columns are identical (meeting Pauli exclusion principle, no two electrons can have same orbital and spin)

Let's see what happens if we apply this approach to a general molecular system

General N-electron system, closed shell (Leach sec 2.4.2):

$$E = 2 \sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} 2(J_{ij} - K_{ij}) \quad (\text{Leach eq. 2.106, 2.107, 2.110, 2.120})$$

where

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NOTE: Switched to reduced (atomic) units

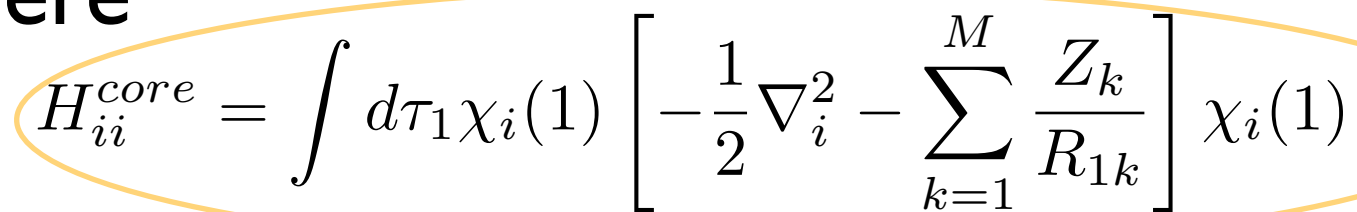
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and results from Pauli -- electrons of same spin can't be in same state

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Well, now we have an expression for the energy, which is fine, but how do we get the wavefunctions and orbitals?

- Remember: No single “correct” solution since it can’t be solved analytically

- Apply variational theorem from some reasonable starting point

- Let’s just combine analytic atomic orbitals from hydrogen atom (LCAO: linear combination of atomic orbitals)

$$\chi_i = \left[\sum_u c_{ui} \phi_u \right] s_i \quad \text{with } \phi_u \text{ the wavefunctions for H}$$

- Optimize coefficients c_{ui}
- How do we optimize? Find the minimum energy set of coefficients: $\frac{\partial E}{\partial c_{ui}} = 0$

This results in a big nasty equation which
has to be solved “self-consistently”

That was Hartree-Fock: Why isn't this the end of the story on QM?

- Number of orbitals required:
 - Minimum number of orbitals is equal to the number of electrons in the system. More allows treatment of unoccupied energy levels, can enhance accuracy
- Mean-field approximation:
 - More importantly: It is a mean-field solution, which means that each electron moves in the average field due to the presence of the other electrons

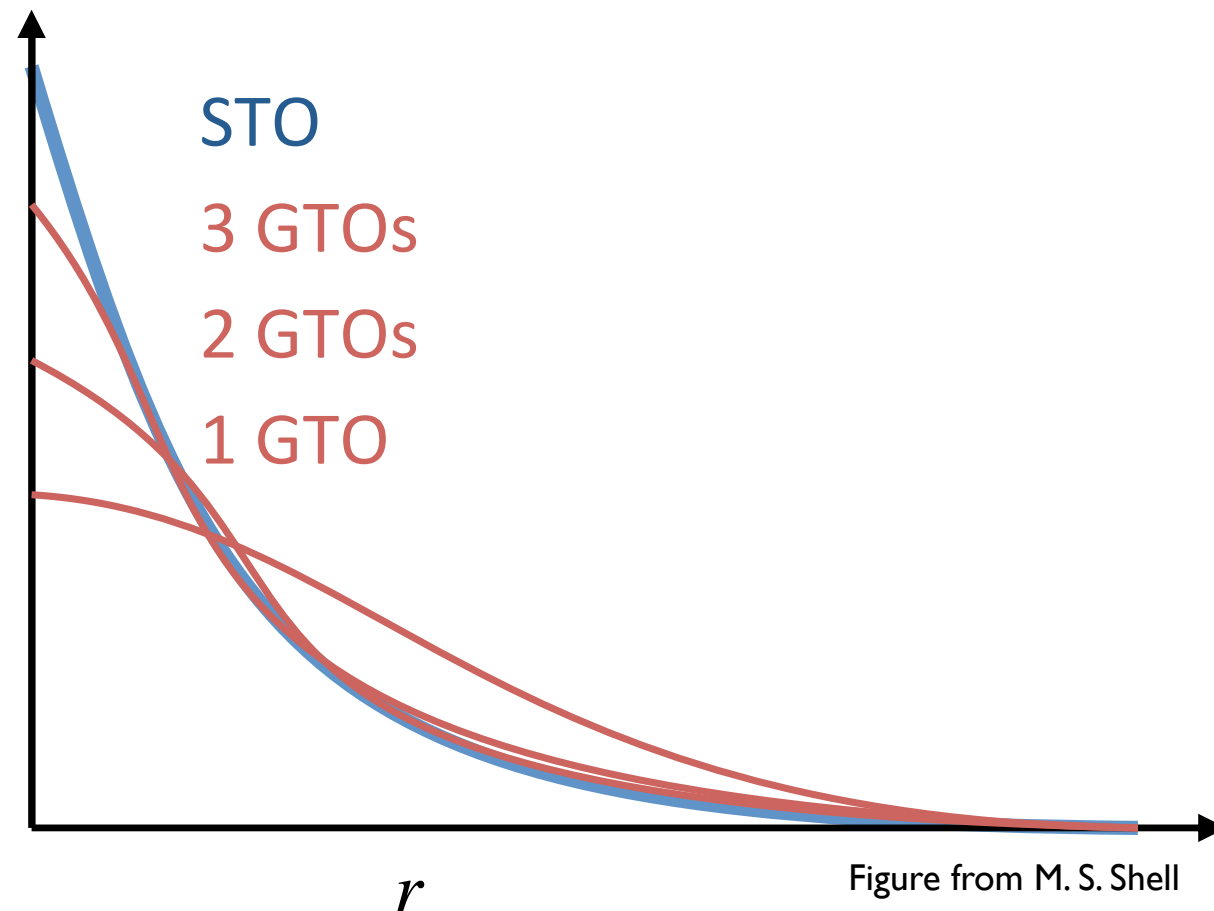
Also, there are numerical challenges relating to ‘basis sets’

- The radial functions involve Laguerre polynomials, which have a complicated functional form
- Slater suggested instead using orbitals of the form

$$R_{nl}(r) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\zeta r}$$

- These are called “Slater-type orbitals” (STO) and follow the Laguerre polynomials reasonably well
- But these are hard to use too
 - Hard to deal with orbitals centered at different nuclei
- Instead of the STOs, Gaussians are often used instead to approximate the STOs

Gaussian-type orbitals (GTOs) approximate the STOs well fairly quickly



Gaussians are easy to work with because the product of two Gaussians centered in different places is just another Gaussian

- Makes the calculations very fast

Brief overview of some basis sets

- **STO- n G:**
 - Minimal basis sets using n Gaussian functions to represent STO; 3 is the absolute minimum for n .
 - Minimal in that they use only a single s-type function for hydrogen, only 1s, 2s, and 2p for lithium to neon, etc.
 - Useful for quickly computing geometries, but limited accuracy
- **3-21G:**
 - Three Gaussians for core orbitals
 - Split basis set for valence electrons: Two for contracted part, one for diffuse
- **6-31G:**
 - Same as above, six gaussians for core, four for valence. More accurate.

Basis sets continued

- **6-31G*:**
 - Same as above, but allowing polarization (distortion) of non-hydrogen orbitals
 - i.e. a polar hydrogen atom should attract extra electron density at neighboring atoms
 - ** version adds polarization on hydrogens also
 - Relatively standard moderate-accuracy calculation (used for many force fields) but tends to be overpolarized
- **Anions and molecules with lone pairs present challenges**
 - “+” basis sets add diffuse functions further out, i.e. 3-21+G, 6-31+G*
- **Complete basis set limit:**
 - Increasing the size of the basis set can change results; ultimately, this should stop at the complete basis set limit, where results have reached their final value for the particular calculation

Computing the electron density

- Electron density closely related to important properties:
 - Dipole and multipole moments
 - Starting point for developing fixed-charged models
- $\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$
- **Note** $N = \int \rho(\mathbf{r}) d\mathbf{r}$
- If written as a sum of basis functions, then:

$$\rho(\mathbf{r}) = \sum_{u=1}^K \sum_{v=1}^k \left(\sum_{i=1}^N c_{ui} c_{vi} \right) \phi_u^*(\mathbf{r}) \phi_v(\mathbf{r})$$

Summary of Hartree-Fock

- Approximate the wavefunction as a product of wavefunctions for individual electrons
- Expand these wavefunctions in terms of hydrogen-like basis functions
- Approximate these as a sum of Gaussian-type orbitals with coefficients chosen to reproduce Slater-type orbitals
- Optimize coefficients self-consistently to find the minimum energy, subject to orthonormality
- Compute physical properties such as electron density from resulting wavefunctions

Density functional theory is concerned only with the electron density, not the wavefunction

- Hohenberg and Kohn: Ground state energy and other properties are uniquely determined by a *functional* of the electron density: $E_0 [\rho(\mathbf{r})]$
 - Square brackets denote functional: It depends on complete behavior of density, not density at a particular point
 - i.e. $F[y] = \int y(x)d(x)$ is a functional of y
- Kohn & Sham: This can be written as
$$E [\rho(\mathbf{r})] = \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{KE}[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

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Interaction with external potentials (nuclei)

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

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KE (approximation: for noninteracting electrons)

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

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Hartree term (electron-electron repulsion)

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

Exchange-correlation term is not known exactly, but it is universal

- There are a variety of approximations for it
 - Simplest is the Local Density Approximation (LDA): $E_{XC}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\epsilon_{xc}(\rho(\mathbf{r}))d\mathbf{r}$
 - Only the local electron density affects the exchange-correlation energy in this approximation
 - ϵ_{xc} often from simulations of homogeneous electron gas
 - Sometimes fitted, for example one proposal:

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

Solving for the density involves finding the density that minimizes the energy

- To find the minimum, we set $\frac{\delta}{\delta\rho(\mathbf{r})} \left[E[\rho(\mathbf{r})] - \mu \int \rho(\mathbf{r}) d\mathbf{r} \right] = 0$

- μ is a constant (Lagrange multiplier) ensuring normalization

- To solve, we write in terms of orbital equations:

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

- Evaluating the minimization gives the Kohn-Sham equation:

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

- Solved self-consistently: (1) Guess initial density
- (2) Derive orbitals, like in Hartree-Fock
- (3) Update density
- Iterate 2-3 until converged

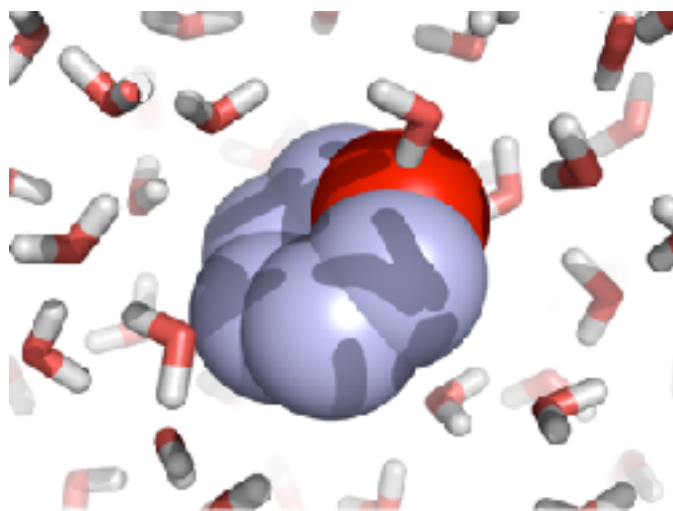
Ab initio molecular dynamics

- Car and Parrinello strategy moves nuclei along with electrons, allowing motion of whole system
 - So far we examined only properties for fixed nuclear positions
- Sets up equations of motion for coefficients
 - Approximately follow the orbital coefficients one would find from a DFT solution to the electronic structure for each nuclear position
 - Choosing fictitious “masses” for the coefficients allows this to reproduce the time-evolution of the electronic structure along with motions of nuclear positions
- Ab initio calculations are very expensive
 - Only ~ 100 atoms feasible
 - Car-Parinello dynamics, up to around 10 ps.
 - Expense scales roughly as $\sim N^4$

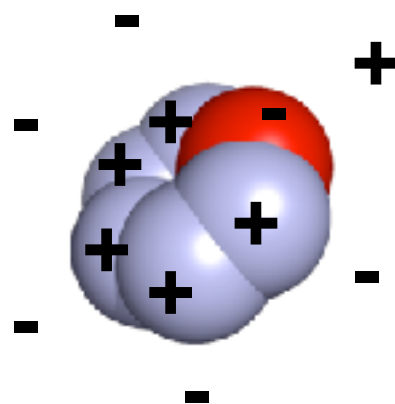
Semi-empirical methods

- Semi-empirical methods achieve better speeds and scaling than HF and DFT approaches
- Only treat valence electrons explicitly
- Have many parameters fitted to experimental data to make up for missing details
- Can treat ~ 1000 atoms and longer timescales (ns)
- Large parameter sets are required
 - Subject to overparameterization in some cases?
 - Often neglect dispersion interactions?

Most chemistry doesn't happen in the gas:
Continuum solvent models try to capture this



- Explicit solvent



- Continuum solvent models

One important effect: Molecules are more polarized in solution than in vacuum

But also: We might be interested in predicting
solvation/solubility