Contents

1 Introduction

1.1 What do we care about?

Things chemistry/materials-related:

- What are the properties of atoms?

- What molecules do they make? What other substances do they make?

- What are the shapes of those molecules? Structures of those solids? Properties of them?

- How do those substances react with each other?

- What are the energies of those reactions?

- What are the rates of those reactions?

- What is the strongest substance?

- How do we make a substance to do. . . .?

- add your own questions. . . .

Things that relate to the *chemical* properties of substances.

1.2   How are we going to figure these out? With only a computer?

1926 Erwin Schrödinger equation: $\hat{H}\Psi = E\Psi$

1929 Paul Dirac, British physicist

> The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus *completely known*, and the difficulty lies only in the fact that application of these laws leads to equations that are *too complex to be solved.*

> It therefore becomes desirable that *approximate practical methods* of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

1930's-1950's Elaboration, analytical applications

1950's Computers start to appear for technical applications

1960's Density functional theory emerges.

1960's-1970's Numerical solutions of Schrödinger equation for atoms/molecules—expert users

1980's "Supercomputer" era—routine use of computational chemistry software becomes possible

Figure 1: Ohio State Cray Y-MP supercomputer, ca. 1989. World's fastest computer at the time. 333 MFlop top speed, 512 Mb RAM

1990's "Chemical accuracy" era—very precise solutions routinely available, for a cost! See Schneider, *JPC* **1994**.

1990's Density functional theory (DFT) allows applications to solids/surfaces/liquids to become common. See Hass, *Science,* **1998**

1990's Visualization moves to the desktop

2000's Computational "screening," materials discovery (Gurkan, *J. Phys. Chem. Lett.,* **2010**), materials genome (https://materialsproject.org/).

Today Computational chemistry widely integrated into all aspects of chemical, materials, biological research

`Computational chemistry` is now so vast it is impossible to cover everything completely. We limit ourselves to quantum-mechanics-based calculations.

1.3 Our goals

1. Understand when it is appropriate to use quantum-mechanics methods.

2. Be able to state the basic theoretical, mathematical, and numerical concepts behind quantum mechanical "wavefunction theory" (WFT) and "density functional theory," (DFT) calculations.

3. Understand the terminology and practical issues associated with doing quantum chemical simulations.

4. Get hands-on experience with these concepts using popular computational tools of today, including GAMESS for molecular systems and Vasp for condensed phase systems.

5. Learn how to set up, execute, and analyze results in a modern, Python notebook environment.

6. Learn how to apply the results of quantum chemical simulations to calculate things you care about.

7. Demonstrate an ability to formulate a problem and apply QM methods to it.

8. Develop the skills to understand a literature paper in the area.

1.4 Reading resources

- These notes

- Chris Cramer, *Essentials of Computational Chemistry*, Wiley, 2004

- Martin, *Electronic Structure*, Cambridge, 2004

- Sholl and Steckel, *Density Functional Theory: A Practical Introduction*, Wiley, 2009

- Kitchin book, http://kitchingroup.cheme.cmu.edu/dft-book/

1.5 Software tools

1.5.1 Notebooks

- jupyter/ipython

- emacs/org-mode

1.5.2 Molecular methods

- Avogadro environment http://avogadro.cc/wiki/Main_Page

- GAMESS code http://www.msg.ameslab.gov/GAMESS/GAMESS.html

1.5.3 Supercell methods

- Vasp code http://www.vasp.at/

- ASE environment https://wiki.fysik.dtu.dk/ase/

1.5.4 Great for getting started

- Webmo <http://www.webmo.net/>

2 Refresher on Quantum Mechanics

2.1 Why quantum mechanics?

Want to describe "mechanics" (equations of motion) of atomic-scale things, like electrons in atoms and molecules

Why? These ultimately determine the energy, the shape, and all the properties of matter.

de Broglie wavelength (1924)

$$\lambda = h/p = h/mv \tag{1}$$

$$h = 6.626 \times 10^{-34} \, \mathrm{J\,s} \text{(Planck's constant)} \tag{2}$$

	Car	Electron
mass m	$1000\,\mathrm{kg}$	$9.1 \times 10^{-31}\,\mathrm{kg}$
velocity v	$100\,\mathrm{km/hr}$	$0.01\,\mathrm{c}$
	typical value on the highway	typical value in an atom
momentum p	$2.8 \times 10^{-4}\,\mathrm{kg\,m/s}$	$2.7 \times 10^{-24}\,\mathrm{kg\,m/s}$
wavelength λ	$2.4 \times 10^{-38}\,\mathrm{m}$	$2.4 \times 10^{-10}\,\mathrm{m}$
	too small to detect. Classical!	Comparable to size of an atom. *Must* treat with QM!

How to describe wave properties of an electron? Schrödinger equation (1926)

$$\text{Kinetic energy} + \text{Potential energy} = \text{Total Energy}$$

Expressed as differential equation (Single particle, non-relativistic):

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t) = -i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) \tag{3}$$

If the potential V is time-invariant, can use separation of variables to show that the steady-state, time-independent solutions are characterized by an energy E and described by:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4}$$

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar} \tag{5}$$

2.2 Postulates of non-relativistic quantum mechanics

2.3 Notes on constants and units

Resource on physical constants: http://physics.nist.gov/cuu/Constants/ Resource for unit conversions: http://www.digitaldutch.com/unitconverter/

Unit converter available in Calc mode in Gnu emacs **highly recommended**

Energy units $1\,\mathrm{eV} = 1.602\,18 \times 10^{-19}\,\mathrm{J} = 96.485\,\mathrm{kJ/mol} = 8065.5\,\{\mathrm{cm}^{-1}\} = 11\,064\,\mathrm{K\,k_B}$

Table 1: Postulates of Non-relativistic Quantum Mechanics

Postulate 1: The physical state of a system is completely described by its wavefunction
Ψ**.** In general, Ψ is a complex function of the spatial coordinates and time. Ψ is required to be:

   I. Single-valued
  II. continuous and twice differentiable
 III. square-integrable ($\int \Psi^* \Psi d\tau$ is defined over all finite domains)
  IV. For bound systems, Ψ can always be normalized such that $\int \Psi^* \Psi d\tau = 1$

Postulate 2: To every physical observable quantity M there corresponds a Hermitian operator $\hat{M}$. **The only observable values of M are the eignevalues of $\hat{M}$.**

Physical quantity	Operator	Expression
Position x, y, z	$\hat{x}, \hat{y}, \hat{z}$	$x\cdot, y\cdot, z\cdot$
Linear momentum $p_x, \ldots$	$\hat{p}_x, \ldots$	$-i\hbar \dfrac{\partial}{\partial x}, \ldots$
Angular momentum $l_x, \ldots$	$\hat{p}_x, \ldots$	$-i\hbar \left(y \dfrac{\partial}{\partial z} - z \dfrac{\partial}{\partial y} \right), \ldots$
Kinetic energy T	$\hat{T}$	$-\dfrac{\hbar^2}{2m}\nabla^2$
Potential energy V	$\hat{V}$	$V(\mathbf{r}, t)$
Total energy E	$\hat{H}$	$-\dfrac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)$

Postulate 3: If a particular observable M is measured many times on many identical systems is a state Ψ, the average resuts with be the expectation value of the operator $\hat{M}$:

$$\langle M \rangle = \int \Psi^* (\hat{M}\Psi) d\tau$$

Postulate 4: The energy-invariant states of a system are solutions of the equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t)$$
$$\hat{H} = \hat{T} + \hat{V}$$

The time-independent, stationary states of the system are solutions to the equation

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Postulate 5: (The **uncertainty principle**.) Operators that do not commute ($\hat{A}(\hat{B}\Psi) \neq \hat{B}(\hat{A}\Psi)$) are called *conjugate*. Conjugate observables cannot be determined simultaneously to arbitrary accuracy. For example, the standard deviation in the measured positions and momenta of particles all described by the same Ψ must satisfy $\Delta x \Delta p_x \geq \hbar/2$.

Table 2: Atomic units common for quantum mechanical calculations (see `http://en.wikipedia.org/wiki/Atomic_units`)

	Atomic unit	SI unit	Common unit
Charge	$e = 1$	1.6021×10^{-19} C	
Length	$a_0 = 1$ (bohr)	5.29177×10^{-11} m	0.529177 Å
Mass	$m_e = 1$	9.10938×10^{-31} kg	
Angular momentum	$\hbar = 1$	1.054572×10^{-34} J s	
Energy	$E_h = 1$ (hartree)	4.359744×10^{-18} J	27.2114 eV
Electrostatic force	$1/(4\pi\epsilon_0) = 1$	8.987552×10^{-9} N m^2/C^2	
Boltzmann constant		1.38065×10^{-23} J/K	8.61733×10^{-5} eV/K

2.4 Example: Energy states of a particle in a box

System defined by potential experienced by particle:

$$V(\mathbf{r}) = 0, \qquad 0 < x, y, z < L$$

$$V(\mathbf{r}) = \infty, \qquad x, y, z \leq 0, \ x, y, z \geq L$$

3D box $\rightarrow$ 3 degrees of freedom/coordinates

Schrödinger equation

$$-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z) \tag{6}$$

$$\psi(x,y,z) = 0, \quad x,y,z \leq 0, \ x,y,z \geq L \tag{7}$$

A second-order, linear, partial differential equation. Boundary value problem. Solve by separation of variables. Postulate $\psi(x,y,z) = X(x)Y(y)Z(z)$. Substituting and rearrange to get

$$-\frac{\hbar^2}{2m_e}\left(\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)}\frac{\partial^2 Z(z)}{\partial z^2}\right) = E \qquad 0 < x,y,z < L \tag{8}$$

ftn x + ftn y + ftn z = constant $\rightarrow$ each term must be constant.

Equation for each dimension

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2 X(x)}{\partial x^2} = E_x X(x), \qquad X(0) = X(L) = 0 \tag{9}$$

Seek function that twice differentiated returns itself and satisfies boundary conditions.

$$X(x) = \sin\frac{n_x \pi x}{L}, \qquad n_x = 1, 2, 3, \ldots \tag{10}$$

$$E_{n_x} = \frac{n_x^2 \pi^2 \hbar^2}{2m_e L^2} \tag{11}$$

Solutions called *eigenfunctions* (or *wavefunctions*) and *eigenvalues*. Characterized by *quantum numbers*, one for each degree of freedom. These (and all QM) solutions have certain special properties, including that they *orthonormal* and form a *complete set*.

Normalization

Seek a constant such that the inner eigenfunction product is unity.

$$C^2 \int_0^L \sin^2\frac{n_x \pi x}{L} dx = C^2 L/2 = 1 \to C = \pm\sqrt{\frac{2}{L}} \tag{12}$$

$$X(x) = \pm\sqrt{\frac{2}{L}}\sin\frac{n_x \pi x}{L}, \qquad n_x = 1, 2, 3, \ldots \tag{13}$$

Orthonormal

$$\langle X_{n_x}|X_{n_x'}\rangle = \delta_{n_x, n_x'} \qquad \text{Dirac notation} \tag{14}$$

Energies and wavefunctions of an electron confined to a 1 nm box

- Energy increase with number of *nodes.*

- Is this real? See Ho, *J. Phys. Chem. B* **2005**, *109*, 20657. Where *is* the electron?

Complete set Any function on the same domain that satisfies the same boundary conditions can be represented as a linear combination of these solutions:

$$f(x) = \sum_i \left\{ \int_0^L X_i(x) f(x) dx \right\} X_i(x) = \sum_i C_i X_i(x) \tag{15}$$

$$|f\rangle = \sum_i |X_i\rangle\langle X_i|f\rangle \quad \text{Dirac notation} \tag{16}$$

Illustrates idea of a basis set. These functions are the basis in "plane wave" supercell methods.

Three-dimensional solutions

$$\psi(x,y,z) = X(x)Y(y)Z(z) = \left(\frac{2}{L}\right)^{3/2} \sin\frac{n_x\pi x}{L} \sin\frac{n_y\pi y}{L} \sin\frac{n_z\pi z}{L}, \qquad n_x, n_y, n_z = 1, 2, 3, \ldots \tag{17}$$

$$E = E_x + E_y + E_z = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2\hbar^2}{2mL^2} \tag{18}$$

Two-dimensional particle in a box, $n_x = n_y = 1$

Two-dimensional particle in a box, $n_x = n_y = 2$

Properties of solutions:

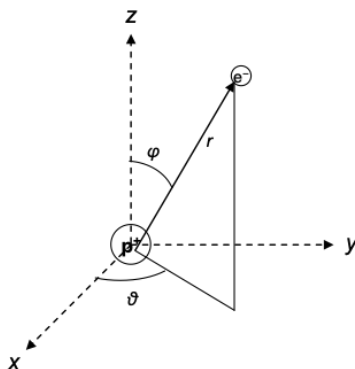- Symmetry of system introduces degeneracy in solutions

Figure 2: Energy sates of 3D Particle in a box

- Energy depends on volume $\rightarrow$ pressure!

3 Hydrogen atom: simplest chemical "thing"

3.1 Schrödinger equation

Place massive nucleus at origin and describe position of electron in spherical coordinates

$$\left\{ -\frac{\hbar^2}{2m_e}\nabla^2 + V(r) \right\} \psi(\boldsymbol{r}) \;\; = \;\; E\psi(\boldsymbol{r}) \tag{19}$$

$$V(r) \;\; = \;\; -\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{r}|} \tag{20}$$

Coulomb potential—our nemesis! Decays slowly with distance. Boundary conditions?

3.2 Analytical solutions

1. Separate: $\psi(r,\theta,\phi) = R(r)\Theta(\theta,\phi)$

2. Angular equation $\hat{L}^2\Theta(\theta,\phi) = E_L\Theta(\theta,\phi)$

   (a) $\Theta = Y_{lm_l}(\theta,\phi)$ are "spherical harmonics", describe angular motion

   (b) Azimuthal quantum number $l = 0, 1, ..., n-1$, correspond to s, p, d, ... orbital sub-shells; angular "shape," number of angular nodes, angular momentum of electron

   (c) Magnetic quantum number $m_l = -l, -l+1, ..., l, \ldots$ orientation of orbital

3. Radial equation

$$\left\{ -\frac{\hbar^2}{2m_e}\frac{d}{dr^2} + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \right\} rR(r) = ErR(r)$$

Solutions are a polynomial * exponential decay. Exponential part called a *Slater* function. Larger the exponent, faster the decay. Degree of polynomial determined by principle quantum number $n = 1, 2, \ldots$.

Energy expression, corresponds to our conventional H atom spectrum

$$E_n = -\frac{1}{n^2}\left(\frac{e^2}{2a_0}\right) = -13.6\,\text{eV} \cdot \frac{1}{n^2}, \qquad n = 1, 2, \ldots$$

Table 3: Hydrogen atom

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, 0 < r < \infty$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left\{\frac{1}{r^2}\left[\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right] - \frac{\hat{L}^2}{\hbar^2 r^2}\right\} + V(r)$$

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]$$

$$\psi(r,\theta,\phi) = R(r)Y_{l,m_l}(\theta,\phi)$$

$$\left\{-\frac{\hbar^2}{2m_e}\frac{d}{dr^2} + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right\}rR(r) = ErR(r)$$

$$R_{nl}(r) = N_{nl}e^{-x/2}x^l L_{nl}(x), \quad x = \frac{2r}{na_0}$$
$$P_{nl}(r) = r^2 R_{nl}^2$$

$$n = 1, 2, \ldots, \quad l = 0, \ldots, n-1 \quad m_l = 0, \pm 1, \ldots, \pm l$$

$$N_{nl} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}$$

$$L_{10} = L_{21} = L_{32} = \ldots = 1 \quad L_{20} = 2 - x \quad L_{31} = 4 - x$$

$$E_n = -\frac{1}{2}\frac{\hbar^2}{m_e a_0^2}\frac{1}{n^2} = -\frac{E_H}{2}\frac{1}{n^2}$$

$$|L| = \hbar\sqrt{l(l+1)}, L_z = m_l\hbar$$

$$\langle r \rangle = \left\{\frac{3}{2}n^2 - \frac{1}{2}l(l+1)\right\}\frac{a_0}{Z}$$

Questions: Ionization energy of an H atom? $1s \to 2s$ energy? Thermal populations?

Integrate out angular components to get radial probability function $P_{nl}(r) = r^2 R_{nl}^2(r)$

$$\langle r \rangle = \int r P_{nl}(r) dr = \left(\frac{3}{2} n^2 - l(l+1) \right) a_0$$

Note darn electron doesn't want to stay in the Coulomb well! Wavefunction extends beyond the classical region defined by $E_n = V(r_{\text{classical}})$. This phenomenon is called *tunneling*, is a purely quantum mechanical effect, is pervasive in chemistry, leading for instance to chemical bonding.
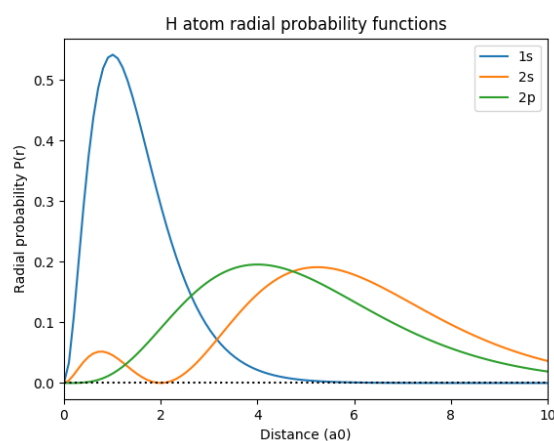

Figure 3: H atom wavefunctions

Figure 4: H atom radial probability

3.3   *Variational principle*

What if we don't know where to look to find the $R(r)$? Or an analytical solution doesn't exist? Solve numerically.

$l = 0$ case, in atomic units:

Figure 5: Pythonic s ($l = 0$), p ($l = 1$), and d ($l = 2$) spherical harmonics. Color scale from red to white to blue corresponds to positive to zero to negative sign of wavefunction.

$$\left\{ -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r} \right\} rR(r) = ErR(r), \quad 0 < r\infty$$

Guess something. Must obey appropriate boundary conditions and be a well-behaved function. For example, a *Gaussian*:

$$g_\xi(r) = e^{-\xi r^2}$$

Let's normalize:

$$N = \left\{ \int_0^\infty g_\xi^2(r)r^2dr \right\}^{-1/2} = 2\left(\frac{8\xi^3}{\pi}\right)^{1/4}$$

$$\tilde{g}_\xi(r) = Ng_\xi(r)$$

Now evaluate energy, say for $\xi = 1$:

$$\langle E \rangle = \langle \tilde{g}_1 | \hat{H} | \tilde{g}_1 \rangle = -0.096 \, \text{Hartree}$$

Hmmm, not very good, much higher in energy than true answer of -0.5 Hartree.

Let's try adding two Gaussians together, with equal weight:

$$b(r) = N_s \left(\tilde{g}_1(r) + \tilde{g}_{0.5}(r) \right)$$

Normalize:

$$
\begin{align}
\langle b(r)|b(r)\rangle &= N_s^2 \left(\langle \tilde{g}_1|\tilde{g}_1\rangle + \langle \tilde{g}_{0.5}|\tilde{g}_{0.5}\rangle + 2\langle \tilde{g}_1|\tilde{g}_{0.5}\rangle \right) \tag{21} \\
&= N_s(1 + 1 + 2S) = 1 \tag{22} \\
N_s &= \frac{1}{\sqrt{2(1 + S)}} \tag{23}
\end{align}
$$

Note appearance of "overlap integral" $S = \langle \tilde{g}_1 | \tilde{g}_{0.5} \rangle$, shows how similar or different g_i are.

Re-evaluate energy

$$\langle b(r)|\hat{H}|b(r)\rangle = -0.306 \, \text{Hartree}$$

Much closer to the truth!

Could even weight the two Gaussians differently:

$$c(r) = N'_s \left(\tilde{g}_1(r) + 1.5\tilde{g}_{0.5}(r) \right)$$

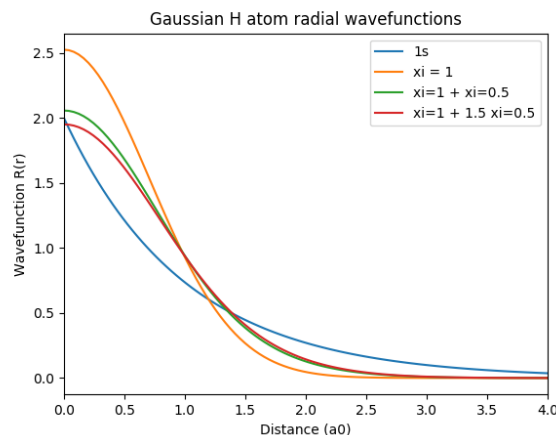$$\langle c(r)|\hat{H}|c(r)\rangle = -0.333\,\text{Hartree}$$

Better yet!

Figure 6: Comparison of exact and approximations 2 H 1s radial function

Could continue to add Gaussians of various exponents, and could vary weights, or could even add in any other functions that we want that are "well-behaved." Would find that no matter what we do, the "model" energy would be greater than the "true" value. Basis of the *variational principle*:

> For any system described by the Hamiltonian $\hat{H}$ and any satisfactory trial wavefunction Ψ,
>
> $$E = \frac{\langle \Psi|\hat{H}|\Psi\rangle}{\langle \Psi|\rangle} \geq E_0$$
>
> where E_0 is the true ground state energy of the system.

Consequence of the completeness of the solutions of the Schrödinger equation. Extremely important to us, because we can use the *calculus of variations* to seek energy-optimal Ψ.

3.4 Basis functions

Recognize that we are approximating

$$R_{10}(r) \approx f(r) = \sum_i c_i \phi_i(r)$$

ϕ_i are *basis functions* and c_i are *variational parameters*, or *coefficients*.

If we find c_i that minimize energy, then we have an optimal approximation to E_0 within our basis, and we are sure that E_0 is an upper bound on the truth. Adding more basis functions /must/lower energy.

Common trade-offs:

1. Want to choose ϕ_i that are good approximation to the "truth"

2. Want to choose ϕ_i that are mathematically convenient

Slaters	Gaussians	Plane waves	Mixed basis
Accurate	Moderate accuracy	Poor accuracy	
Expensive	modest cost	cheap!	
`ADF`	`Gaussian, GAMESS,`	`Vasp, CPMD,`	`FLAPW, CP2k`
	`NWChem, Qchem`	`QuantumEspresso`	

Virtually *all* quantum codes work on this principle, and the main differences are in details of implementation and ancillary functionality provided.

There are exceptions. *GPAW* for instance solves the QM equations by finite difference expressions on a numerical grid. Lends itself to parallelization and may be the future...remains to be seen!

3.5 Secular equations

Apply variational principle to two basis functions for the H atom:

$$f(r) = c_1\phi_1(r) + c_2\phi_2(r)$$

$$\langle E \rangle = \frac{\langle f(r)|\hat{H}|f(r)\rangle}{\langle f(r)|f(r)\rangle}$$

Substitute and solve $\partial\langle E\rangle/\partial c_1 = \partial\langle E\rangle/\partial c_2 = 0$. Each gives a linear *secular equation* in c_1 and c_2:

$$\begin{pmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

where $H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle$ is a *matrix element* and $S_{ij} = \langle\phi_i|\rangle\phi_j\rangle$ is an *overlap*. If $S_{ij} = 0$, basis is *orthogonal*, problem simplifies. If $S_{ij} \approx 1$, basis is *redundant*, not efficient!

Evaluate *secular determinant*

$$\begin{vmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{22} \end{vmatrix} = 0$$

Gives a quadratic in *E*. Yields two solutions, which would be approximations to the *1s and 2s* orbital energies of hydrogen. Back substitution to get coeffients:

$$\begin{array}{ll} \text{1s: } \langle E_{1s}\rangle > E_{1s,\text{true}} & c_1^{1s} \text{ and } c_2^{1s} \\ \text{2s: } \langle E_{2s}\rangle > E_{2s,\text{true}} & c_1^{2s} \text{ and } c_2^{2s} \end{array}$$

Note we always get one solution for each basis function. Secular matrix grows as the square of the number of basis functions, gets expensive to find roots.

If basis is not orthogonal, common to *orthogonalize*. Find linear transformation that makes $\langle S_{ij} = \delta_{ij}$. Evaluate

$$\boldsymbol{c}' = \boldsymbol{S}^{1/2}\boldsymbol{c} \rightarrow \hat{\boldsymbol{H}}' = \boldsymbol{S}^{-1/2}\boldsymbol{H}\boldsymbol{S}^{1/2}$$

$$\begin{pmatrix} H'_{11} - E & H'_{12} \\ H'_{12} & H'_{22} \end{pmatrix} \begin{pmatrix} c'_1 \\ c'_2 \end{pmatrix} = 0$$

$$\boldsymbol{H'c'} = E\boldsymbol{c'}$$

Secular equations reduce to standard linear eigenvalue problem. All the tricks of linear algebra can be applied to find the *eigenvalues* (orbital energies) and *eigenvectors* (wavefunctions). Called *diagonalizing* the matrix. Tricks can be used to find the lowest energy roots only.

Same basic idea is used in virtually all calculations on atoms, molecules, ... Basis of *semi-empirical* and *first principles* methods.

3.6 Spin

Can't leave the H atom without mentioning electron *spin*. Non-relativistic QM gives us three quantum numbers. Relativity teaches that space and time are equivalent. Relativistic H atom solutions introduce a 4th degree of freedom that, under many circumstances, decouples from other three. Call it the electron *spin*, because it behaves like the electron has an intrinsic quantum angular momentum with magnitude $s = 1/2$.

$$m_s = +1/2, \quad \text{``spin up''}, \quad \alpha$$

$$m_s = -1/2, \quad \text{``spin down''}, \quad \beta$$

m_s specifies z component of angular momentum, $s_z = m_s\hbar$.

To fully specify state of H atom, must specify all four quantum numbers.

4 (Two is too) many electrons

Helium: next (after hydrogen) simplest atom

In a sense, we "know" the answer... $1s^2$. But is this same $1s$ as H? No! Different nuclear charge, interactions between the two electrons. This is an approximation and a very convenient shorthand!

4.0.1 Schrödinger equation for He

Wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$, atom energy E.

Define 1-electron operator for each electron, in atomic units. Include kinetic energy of electron and its attraction to nucleus of charge $Z = 2$:

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{|\mathbf{r}_i|}$$

Looks similar to hydrogen atom.

BUT, electrons also repel. Total Schrödinger equation for He:

$$\left\{ \hat{h}_1 + \hat{h}_2 + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \right\} \Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)$$

Last term accounts for electron-electron electrostatic repulsion. Makes problem non-separable and really hard to solve. (How many solutions are there?)

Generalize to n-electron atom, in atomic units:

$$\hat{H} \;=\; \sum_i \hat{h}_i + \sum_{j>i+1} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} \tag{24}$$

$$\hat{H}\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n) \;=\; E\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n) \tag{25}$$

First summation over all electrons, second gets all electron pairs.

Solutions are many-dimensional functions of the coordinates of all the electrons. Cannot solve this analytically, although approaches exist (eg quantum Monte Carlo) that can in principle get very close. Thankfully, though, we can make approximations that work out really well. We'll look at three historically important ones.

4.1 The Hartree atom

Simplest approach is to approximate Ψ. Douglas Hartree (1897-1958) writes:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \approx \psi_1(\mathbf{r}_1) \cdot \psi_2(\mathbf{r}_2)$$

So-called Hartree product. Can't be right. It gives the probability of two electrons being in the same place as some number > 0! Neglects *electron correlation*. How to apply?

1. Apply variational principle: What's the best possible set of ψ_i? We'll say best are the set that give the lowest expectation value of energy.

$$\langle E \rangle \;=\; \langle\Psi|\hat{H}|\Psi\rangle / \langle\Psi|\Psi\rangle \tag{26}$$

$$\frac{\delta\langle E \rangle}{\delta\psi_i} \;=\; 0, \forall i \tag{27}$$

2. Lagrange multipliers to impose orthonormality constraint on ψ_i:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{28}$$

$$L = \langle E \rangle - \sum_{i,j} \epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right) \tag{29}$$

$$\delta L = 0 \tag{30}$$

3. Coupled, one-electron Hartree eigenvalue equations for energy-optimal ψ_i:

$$\left\{ \hat{h}_i + \hat{v}_i^{\text{Hartree}} \right\} \psi_i(\mathbf{r}_1) = \epsilon_i \psi_i(\mathbf{r}_1) \tag{31}$$

$$\hat{v}_i^{\text{Hartree}}(\mathbf{r}_i) = \sum_{j \neq i} \int |\psi_j(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_2 \tag{32}$$

Have to solve this for all n electrons of an atom/molecule. "Hartree potential" represents Coulomb repulsion between electron i and all other electrons, *averaged* over position of those electrons. Always positive. This is a *mean field* approximation. Note appearance of "one electron" energies, ϵ_i, kinetic energy plus repulsion of electron with all others. Total energy is sum of these ϵ_i corrected to avoid overcounting repulsions:

$$\langle E \rangle = \sum_i \epsilon_i - \frac{1}{2} \sum_i \langle \psi_i | \hat{v}_i^{\text{Hartree}} | \psi_i \rangle$$

Presents an obvious difficulty. If we don't know ψ_j ahead of time, how can we even construct Hartree equations, let alone solve them? Hartree offered a numerical solution, in the 1930's, called the **self-consistent field (SCF) approach**:

1. Guess an initial set of ψ_i, one for each electron (he did this on a grid, and jumping ahead a bit, allowed each ψ_i to represent two electrons)

2. Construct Hartree potential for each ψ_i

3. Solve the n differential equations for n new ψ_i

4. Compare new to old ψ_i

5. If the same within a desired tolerance, you are done!

6. If not, return to step 2, using new ψ_i, and repeat.

Hartree's father did this by hand for all the atoms of the periodic table, tabulating wavefunctions and energies for all the electrons in each. See Hartree, Douglas R. *The Calculation of Atomic Structures* (1957). For instance, for He, he'd solve one equation, self-consistently, to get one ψ_1, and then combine to get $\Psi(1,2) = \psi_1(1)\alpha(1)\psi_1(2)\beta_2$. Tedious! Qualitatively great, quantitatively not so hot. Mean-field approximation just not so hot.

Nonetheless, basic idea of representing many-body wavefunction in terms of "orbitals," of setting up orbital equations, and solving using a self-consistent procedure, remain today at the heart of virtually all electronic structure calculations. Hurrah Hartree!

> *Note: It would be very cool to write a simple Python code to illustrate the SCF procedure for two electrons in an atom. Could be done on a grid or in a basis. See eg* `http://www.users.csbsju.edu/~frioux/scf/scf-he.pdf`*.*

4.2 The Pauli principle

One big conceptual short-coming of the Hartree model is that it treats the electrons as if they were distinguishable. QM says electrons are indistinguishable. Furthermore, they have a quantized angular momentum, called a spin, that is either up or down, making them fermions.

Pauli principle: The wavefunction of a multi-particle fermion system must be anti-symmetric to coordinate exchange.

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = -\Psi(\boldsymbol{x}_2, \boldsymbol{x}_1)$$

Here the coordinate **x** includes both the position and the spin (up or down, α or β) of the electron.

Sorry Hartree. Can fix for He by writing

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

Hey, gentle reader, check, does this work? Yes! Exchanging the coordinates changes the sign but keeps everything else the same. Normalizing is easy if we take ψ_1 to be normalized and recall that spin functions are orthogonal:

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2}}\psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

Note it is impossible to construct an antisymmetric wavefunction in which both electrons have the same spatial function *and* the same spin. Two electrons cannot have the same space and spin variables.

A-ok!   No-no!

4.3 Slater determinants and Hartree-Fock

Slater determinant a general way to assure that a wavefunction satisfies Pauli principle:

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(n) & \psi_2(n) & \cdots & \psi_n(n) \end{vmatrix} = |\psi_1\psi_2\cdots\psi_n\rangle$$

Swapping rows swaps coordinates and, by rules of determinants, changes sign.

Let's compare. Two spin-paired electrons in two different orbitals:

$$\begin{vmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_2(2)\beta(2) \end{vmatrix} = \psi_1(1)\psi_2(2)\alpha(1)\beta(2) - \psi_2(1)\psi_1(2)\beta(1)\alpha(2)$$

Antisymmetric? What happens when the two electrons have the same spatial coordinate?

Two spin-aligned electrons in two different orbitals:

$$\begin{vmatrix} \psi_1(1)\alpha(1) & \psi_2(1)\alpha(1) \\ \psi_1(2)\alpha(2) & \psi_2(2)\alpha(2) \end{vmatrix} = (\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))\,\alpha(1)\alpha(2)$$

What happens now?

Exchange guarantees that two electrons of same spin cannot be in the same place! No such guarantee for electrons of opposite spin.

4.4 Hartree-Fock equation

Same song and dance:

1. Apply variational principle to Slater determinant. The best ψ_i are those that minimize the expectation value of the energy.

2. Use method of Lagrange multipliers to keep ψ_i orthogonal.

For simplicity, restrict ourself to cases with an even number of electrons N, all spin-paired, so two electrons in every orbital. Let index j run over all occupied orbitals. Arrive at **restricted Hartree-Fock** equations:

$$\left\{\hat{h}_i + \hat{v}_i^{\text{Hartree}} + \hat{v}^{\text{exchange}}\right\}\psi_i(\mathbf{r}_1) = \epsilon_i\psi_i(\mathbf{r}_1) \tag{33}$$

$$\hat{v}_i^{\text{Hartree}}(\mathbf{r}_1) = 2\sum_{j\neq i}\int |\psi_j(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2 \tag{34}$$

$$\hat{v}_i^{\text{exchange}}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = -\psi_j(\mathbf{r}_1)\sum_{j\neq i}\int \psi_j(\mathbf{r}_2)\cdot\psi_i(\mathbf{r}_2)\frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2 \tag{35}$$

Yikes! Slater determinant wavefunction results in appearance of the "exchange" operator, which turns a ψ_i into a ψ_j. Exchange operator is not a simple multiplication. Must be solved self-consistently, and is much harder to do than the simple Hartree expression.

Slight simplification possible, noting that $i = j$ terms cancel out and slightly redefining operators:

$$\left\{\hat{h}_i + \hat{v}_i^{\text{Hartree}} + \hat{v}^{\text{exchange}}\right\}\psi_i(\mathbf{r}_1) = \epsilon_i\psi_i(\mathbf{r}_1) \tag{36}$$

$$\hat{v}^{\text{Hartree}}(\mathbf{r}_1) = 2\sum_{j}\int |\psi_j(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2 \tag{37}$$

$$\hat{v}_i^{\text{exchange}}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = -\psi_j(\mathbf{r}_1)\sum_{j}\int \psi_j(\mathbf{r}_2)\cdot\psi_i(\mathbf{r}_2)\frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2 \tag{38}$$

Now "Hartree potential" is the same for all orbitals/electrons. We can define the "charge density" to be

$$\rho(\mathbf{r}) = 2\sum_{j} |\psi_j(\mathbf{r})^2|$$

(units of charge/unit volume, multiply by e to get a charge). The Hartree potential can be written

$$\hat{v}^{\text{Hartree}}(\mathbf{r}_1) = \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2$$

This is the Coulomb repulsion of an electron with all electrons, *including itself*! Called Poisson equation, well known in classical physics. Because it involves a Coulomb repulsion, will see either $\hat{v}^{\text{Hartree}}$ or $\hat{v}^{\text{Coulomb}}$. I'll often write $\hat{v}^{\text{Coulomb}}[\rho(\mathbf{r})]$, to emphasize that the Coulomb potential is a *functional* of the charge density.

(Just to make sure we are following units around, the Coulomb potential has units of energy/charge, eg in SI it would be J/C and would have $e/4\pi\epsilon_0$ in front.)

The "exchange potential" cancels out the "self-interaction" of an electron with itself, and insures that two electrons of the same spin cannot be in the same place, ie, the wavefunction vanishes whenever the spatial coordinates of two electrons are the same. It cannot be written simply in terms of the charge density.

4.4.1 Basis of wavefunction theory (WFT)

Hartree-Fock model is much better than Hartree alone, widely implemented in codes. Not particularly good by today's standards. However, it is systematic and rigorous, by requiring exact adherence to the Pauli principle, and it can be systematically improved. It is the foundational basis of all wavefunction theory (WFT) models, all of which are characterized by exactly treating exchange. The only approach some people call *ab initio*.

4.5 Hartree-Fock-Slater

In 1951 John Slater introduced an approximation to the Hartree-Fock model that turned out to anticipate a whole new approach to solving the electronic structure problem, called *density functional theory.*

Rewrite exchange part as (and shorten "exchange" to "x"):

$$\hat{v}_i^{\text{x}}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = -\psi_j(\mathbf{r}_1)\sum_j \int \psi_j(\mathbf{r}_2) \cdot \psi_i(\mathbf{r}_2)\frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2 \tag{39}$$

$$= -\psi_j(\mathbf{r}_1)\sum_j \int \psi_j(\mathbf{r}_2) \cdot \psi_i(\mathbf{r}_2)\frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2 \cdot \frac{\psi_i(\mathbf{r_1})\psi_i(\mathbf{r_1})}{\psi_i(\mathbf{r_1})\psi_i(\mathbf{r_1})} \tag{40}$$

$$= -\left[\int \frac{\rho_i^{\text{x}}(\mathbf{r_1};\mathbf{r_2})}{|\mathbf{r}_2 - \mathbf{r}_1|}d\mathbf{r}_2\right]\psi_i(\mathbf{r_1}) \tag{41}$$

$$\rho_i^{\text{x}}(\mathbf{r_1};\mathbf{r_2}) = \sum_j \frac{\psi_i(\mathbf{r_1})\psi_j(\mathbf{r_2})\psi_j(\mathbf{r_1})\psi_i(\mathbf{r_2})}{\psi_i(\mathbf{r_1})\psi_i(\mathbf{r_2})} \tag{42}$$

This looks like the Coulomb expression, but the density thing is different for each orbital i. The "exchange density" does have units of charge density enters in the same way, but with minus sign, to the electron density. Suggests that exchange can be thought of as an electron "hole" around an electron. This exchange density has some special properties:

1. Every electron at any position $\mathbf{r}_1$ has an exchange hole around it equal to one electron of the same spin as itself:

$$\int \rho_i^{\text{x}}(\mathbf{r}_1;\mathbf{r}_2)d\mathbf{r}_2 = 1$$

2. The exchange hole exactly cancels out all electrons of the same spin at the electron location. Ie, it exactly fixes self-interaction:

$$\rho_i^{\text{x}}(\mathbf{r}_1; \mathbf{r}_1) = \sum_j |\psi_j(\mathbf{r})^2|$$

Thus, the Coulomb repulsion felt by an electron is diminished by an exchange hole that follows the electron around, exactly canceling out the charge at its current location. It's not necessarily spherical and is not the same for all orbitals, but the fact that it has these general properties gives hope that it can be approximated somehow.

Hey, I have an idea! (Actually, Slater had an idea.) What if we had a homogeneous (density the same everywhere) gas of electrons, like electrons of a given density ρ in an infinite box? By symmetry the exchange hole would be spherical, and if it must integrate to 1, then it must have a radius (factor of 2 comes from fact we are only including electrons of the *same* spin):

$$R_{\text{hole}} = \left[\frac{4\pi\rho/2}{3}\right]^{1/3}$$

The potential felt by an electron due to this spherical hole is

$$\hat{v}^x = -\frac{1}{2}\int_{\text{sphere}} \frac{\rho}{r}dr = -\left[\frac{9\pi\rho}{4}\right]^{1/3}$$

Now, let's assume that an electron in a real system experiences an exchange hole potential at any point exactly like that of a homogeneous electron gas of the same density at that point. This is the basis of the *Hartree-Fock-Slater* model:

$$\hat{v}^{x,HFS}(\mathbf{r}_1) = -\frac{3}{2}\left[\frac{3\rho(\mathbf{r}_1)}{\pi}\right] - C\rho(\mathbf{r}_1)^{1/3}$$

Some ambiguity as to the right value of the constant C, so sometimes just taken as a parameter.

Can now write the *Hartree-Fock-Slater* equation:

$$\left\{\hat{h} + \hat{v}^{\text{Coulomb}}[\rho] + \hat{v}^{\text{x,HFS}}[\rho]\right\}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

This is **much** simpler to solve than Hartree-Fock equation, because the left hand side is the same for all electrons given a total density $\rho(\mathbf{r})$. Still must be solved iteratively, using the *self-consistent field*.

4.5.1 Notes

1. Exchange potential scales with the total number of electrons around: more electrons (like near a nucleus) means a more compact, denser exchange hole, more electron exchange "screening," a greater decrease in potential energy. Further from nucleus, more diffuse exchange hole, less screening.

2. Screening is not exact, though; does not exactly cancel self-interaction. Clearest in one-electron case: Coulomb and exchange potentials should then exactly cancel, which they evidently do not! HFS energy of an H atom is not exactly 0.5 au!

3. From a computational point of view, the exchange potential goes from being the hard thing to evaluate to being the easy thing. The Coulomb potential takes more effort to evaluate, and tricks are often implemented to simplify that, like fitting the density to an auxiliary basis set. On the other hand, the 1/3 power makes the exchange potential non-analytic, and solution of the HFS equation (and all DFT methods) involves some form of numerical quadrature.

4. How does the HFS model do? Pretty darn well, in particular for calculating the structures of things, and it works nicely for things like metals. Not a bad deal! Way to go, Slater!

5. Another aside: back in the day, the numerical implementations of Xα were very crude and sometimes gave unreasonable results (like linear water!). Slater still sold it very hard, which did not enamor him or all of DFT to the chemical community, although the physics community was far more accepting. For many years DFT was unaccepted by chemists, until solid numerical implementations in codes like `Gaussian` brought it to the mainstream.

4.5.2 Basis of density functional theory (DFT)

Slater's arguments are not rigorous. However, as we will see later, they can be made rigorous. HFS is the very simplest example of a *density functional theory* model, because it is a model built entirely on charge density. Such approach is justifiable.

4.6 Implementations

4.6.1 `GAMESS`

Hartree-Fock method *always* paired with *basis set* methods and implemented in the codes available at http://webmo.net. Example `GAMESS` input for Hartree-Fock Ar:

```
 $CONTRL SCFTYP=RHF RUNTYP=ENERGY ISPHER=1
      ICHARG=0 MULT=1 COORD=CART $END
 $BASIS GBASIS=CCT $END
 $DATA
Ar
OH 1

Ar 18 0.00000000 0.00000000 0.00000000
 $END
```

And for Hartree-Fock-Slater Ar:

```
 $CONTRL SCFTYP= RHF RUNTYP=ENERGY DFTTYP=Slater ISPHER=1
      ICHARG=0 MULT=1 COORD=CART $END
 $BASIS GBASIS=CCT $END
 $DATA
Ar
OH 1

Ar 18 0.00000000 0.00000000 0.00000000
 $END
```

4.6.2 `FDA`

Hartree-Fock-Slater is intrinsically numerical. Historically interesting is the Herman-Skillman code, that solves the problem numerically on a grid. Available to us as the `fda` code, see `https://www.chemsoft.ch/qc/fda.htm` and `./Resources/00READ.ME`.

Ar input:

```
300 0.0001 30.0
50 0.00001 0.10 0.50  0.682 0.0042
18.0 5
1 0 1.0 1.0
2 0 1.0 1.0
2 1 3.0 3.0
3 0 1.0 1.0
3 1 3.0 3.0
```

Output at `./Resources/Ar.out`.
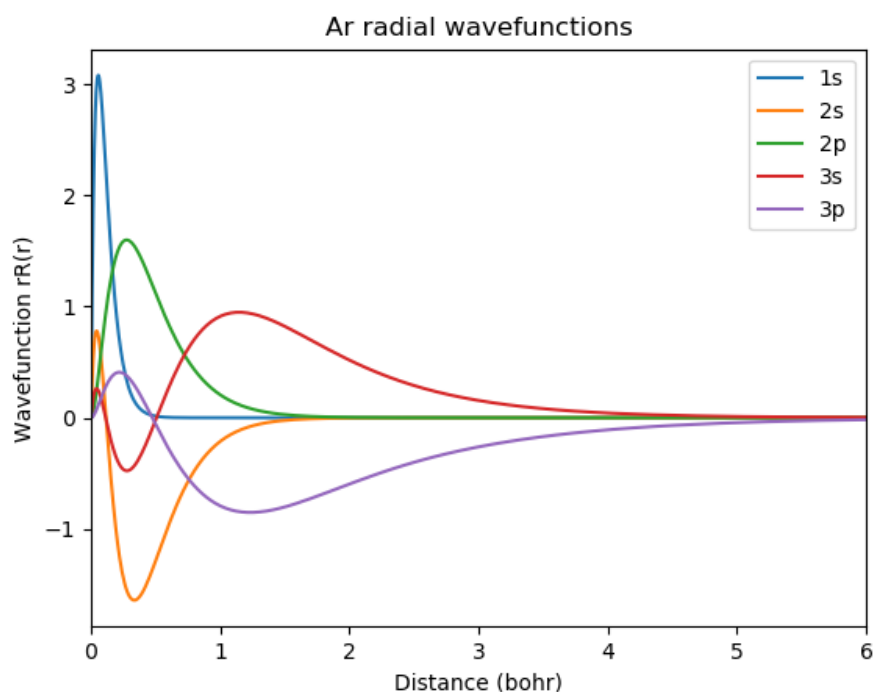
4.7   Performance

One metric is the ability to predict ionization energies.

> Koopman's theorem: The negative of the energy of an occupied orbital $(-\epsilon_i)$) approximates the energy to extract an electron from that orbital, ie to ionize the system. The energy of a virtual orbital approximates the energy to add an additional electron to a system, i.e. the electron affinity. Assumes no relaxation of orbitals.

Figure 7: HFS vs exact ionization energies

4.8 Correlation

If solved to reasonable precision, both the Hartree-Fock and Hartree-Fock-Slater models work pretty darn well for things like the shapes of molecules, structures of solids, charge distributions, vibrational frequencies, ... Don't work so well for computing things that involve making and breaking bonds, like a reaction energy or an activation energy.

Why? All the models discussed here neglect *electron correlation*, the fact that the potential felt by an electron *is* a function of the instantaneous positions of all the other electrons. The contribution of correlation to absolute energies is not big by proportion, but it is very imporant to energy differences. Any "orbital" model cannot capture correlation. It can be introduced systematically and exactly into H-F models (at great computational expense) and systematically and approximately into DFT models (at much more modest expense). Hence the popularity of DFT!

5 Practical electronic structure

5.1 Born-Oppenheimer approximation

In principle all nuclei and electrons should be described quantum mechanically. For H_2, for instance, true wavefunction would be a function of the positions of nuclei and electrons, $\Upsilon(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_\alpha, \mathbf{R}_\beta)$.


Nuclei much heavier than electrons and move much more slowly. Assume nuclei are fixed in space ("clamped") and electrons move in static field of those electrons. Equivalent to assuming that nuclear kinetic energy is decoupled from electron dynamics. Only change is that

$$\hat{h} = -\frac{1}{2}\nabla^2 - \sum_\alpha \frac{Z_\alpha}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|}$$

Schrödinger equation becomes parameteric in nuclear positions; solutions $E(\mathbf{R}_\alpha, \mathbf{R}_\beta)$ define a potential energy surface (PES).

$$E_{\text{PES}}(\mathbf{R}_\alpha, \mathbf{R}_\beta) = E_{\text{Schr}} + \frac{1}{2}\sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\beta - \mathbf{R}_\alpha|}$$
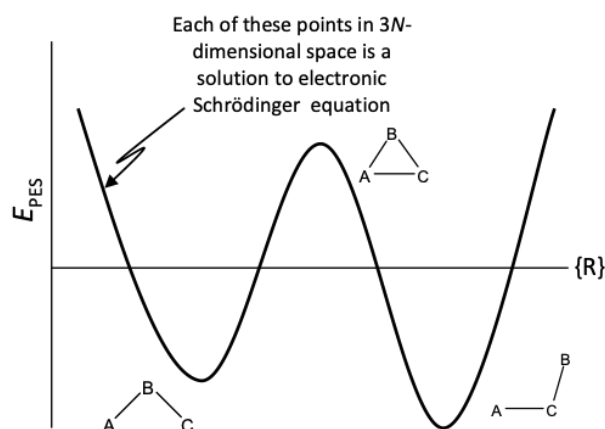
5.2 Model chemistry

Essentially always start with

$$\left\{ \hat{h} + v_{\text{Coulomb}}[\rho] + v_{\text{exchange}}[\psi_i] + v_{\text{correlation}}[\psi_i] \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \tag{43}$$

Standard models of today all treat the one-electron and Coulomb pieces exactly and treat the electron-electron interactions at various levels of approximation.

	v_{exchange}	$v_{\text{correlation}}$	
Wave function theory (WFT)			
Hartree	self-interaction	neglect	historic
Hartree-Fock	exact	neglect	superceded
MPn, CC	exact	perturbative	state-of-the-art
CI	exact	variational	specialized
Density functional theory (DFT)			
Hartree-Fock-Slater	$[\rho^{4/3}]$	neglect	historic
Local density approximation (LDA)	$[\rho^{4/3}]$	$[\rho]$	general purpose solids
Generalized gradient approximation (GGA)	$[\rho, \nabla\rho]$	$[\rho, \nabla\rho]$	general purpose solids/surfaces
"Improved" GGA (RPBE, BEEF, Mxx)	$[\rho, \nabla\rho]$	$[\rho, \nabla\rho]$	general purpose
Hybrid (B3LYP, PBE0, HSE06)	$\approx$ exact	$[\rho, \nabla\rho]$	general purpose molecules specialty solids/surfaces
Meta GGA	$[\rho, \nabla\rho, \nabla^2\rho]$	$[\rho, \nabla\rho, \nabla^2\rho]$	developing

The choice of the electronic structure model is the most fundamental approximation in applying these methods. Determined from experience and need.

Specification in `GAMESS` (https://www.msg.chem.iastate.edu/GAMESS/GAMESS.html) is a bit arcane. Default is Hartree-Fock. To specify DFT model, use

```
$CONTRL DFTTYP =   Slater (HFS), SVWN (LDA), PBE (GGA), B3LYP (Hybrid)
```

5.2.1   Beyond Hartree-Fock

Many methods available. See manual for full description. Most common is second-order perturbation theory, "MP2":

```
$CONTRL MPLEVL=2 $END
```

If you want a very high quality number, have a big computer and time to wait, try "coupled cluster":

```
$CONTRL CCTYP=CCSD(T) $END
```

5.3   Bring back the basis sets

The one-electron equations eq 5.2 give us defining expressions for the energy-optimal orbitals, but they aren't convenient to solve for anything more complicated than an atom. Expand solutions in a basis set:

$$\psi_i(\boldsymbol{r}) = \sum_\nu C_{\mu i}\phi_\nu(\boldsymbol{r})$$

Often atom-centered. You'll see the term "linear combination of atomic orbitals," LCAO.

Abbreviate $\hat{f}\psi_i = \epsilon_i\psi_i$. Substitute in ψ_i, mulitple through by a basis function ϕ_μ:

$$\sum_\nu F_{\mu\nu}C_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu}C_{\nu i}, \qquad \boldsymbol{FC} = \boldsymbol{SC}\epsilon$$

where

$$F_{\mu\nu} = \langle\psi_\mu|\hat{f}|\phi_\nu\rangle \qquad S_{\mu\nu} = \langle\psi_\mu|\phi_\nu\rangle$$

Matrix equation to solve.

Historically interesting, "semi-empirical" methods (MNDO, ...) worked by parameterizing the matrix elements against atom properties.

Recall $\hat{f}$ depends on the density, which can be written

$$\rho(\boldsymbol{r}) = \sum_{\mu\nu} P_{\mu\nu}\phi_\mu(\boldsymbol{r})\phi_\nu(\boldsymbol{r}), \qquad P_{\mu\nu} = 2\sum_i C_{\mu i}C_{\nu i}$$

Depending on implementation, pieces of $\hat{f}$ can often be computed just once and reused, eg one-electron integrals $\langle\phi_\mu|\hat{h}|\phi_\nu\rangle$.

Algorithm:

1. Put your atoms somewhere in space

2. Select a basis

3. Pre-compute what you can

4. Guess some coefficients/density/density matrix

5. Construct secular matrix elements

6. Solve secular matrix equation for C and ϵ

7. Construct and compare new density to old

8. Update density and repeat, or ...

9. ...if less than tolerance, all done!

ALWAYS check to be sure result has converged, to the state you want!

5.4 H2O Energy Example

Hartree-Fock calculation on H_2O, minimal (STO-3G) basis set.

```
!   File created by the GAMESS Input Deck Generator Plugin for Avogadro
 $BASIS GBASIS=STO NGAUSS=3 $END
 $CONTRL SCFTYP=RHF RUNTYP=ENERGY COORD=CART $END
 $DATA
Title: H2O energy evaluation
C1
O    8.0    -0.89600     3.13196     0.00000
H    1.0     0.07400     3.13196     0.00000
H    1.0    -1.21933     3.71670     0.70316
 $END
```

See ./Resources/H2O-STO3G.gamout.

5.5   Symmetry

Often problem can be simplified by taking advantage of symmetry of the system.

```
!   File created by the GAMESS Input Deck Generator Plugin for Avogadro
 $BASIS GBASIS=STO NGAUSS=3 $END
 $CONTRL SCFTYP=RHF RUNTYP=ENERGY COORD=CART $END
 $DATA
Title: H2O energy evaluation
CNV 2

O     8.0    -0.89600     3.13196     0.00000
H     1.0     0.07400     3.13196     0.00000
H     1.0    -1.21933     3.71670     0.70316
 $END
```
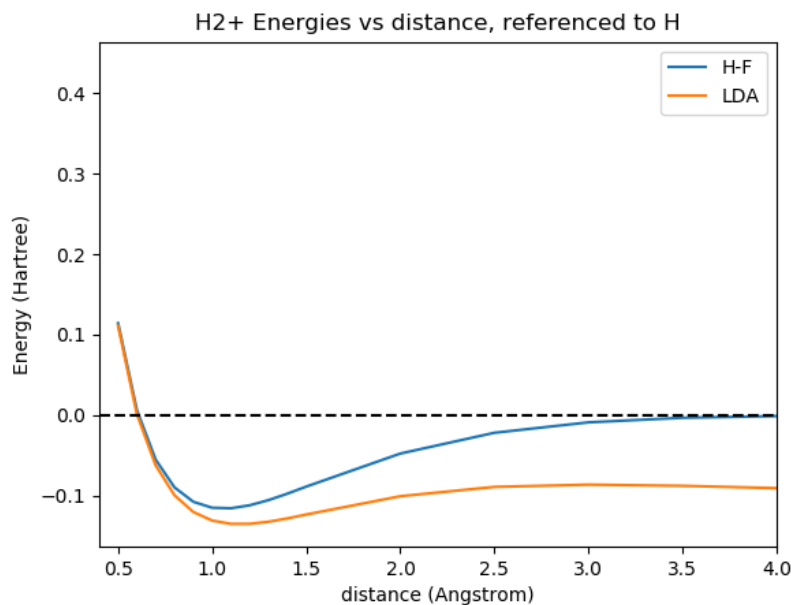
Results get labeled by symmetry labels.

See `./Resources/H2O-C2V.gamout`.

5.6   Examples

5.6.1   Dissociating H2+ example

Compute energy vs distance. Should dissociate to H atom and H^+ ion.


Oops, come on, LDA! Illustrates self-interaction problem in LDA. Electron is too eager to be diffuse, spreads out over both atoms when it should localize on one.

5.6.2 Dissociating HHe+ example

Compare Hartree-Fock and LDA for $H-He^+$ vs distance. (Isoelectronic to H_2, but avoids any problems with symmetry. Should dissociate to H^+ and He. Does it?

```
 $BASIS GBASIS=STO NGAUSS=3 $END
 $CONTRL SCFTYP=RHF RUNTYP=ENERGY ICHARG=1 MULT=1 $END
 $DATA
Title
C1
H     1.0     0.   0.  0.
He    2.0     0.   0.  XXX
 $END
```
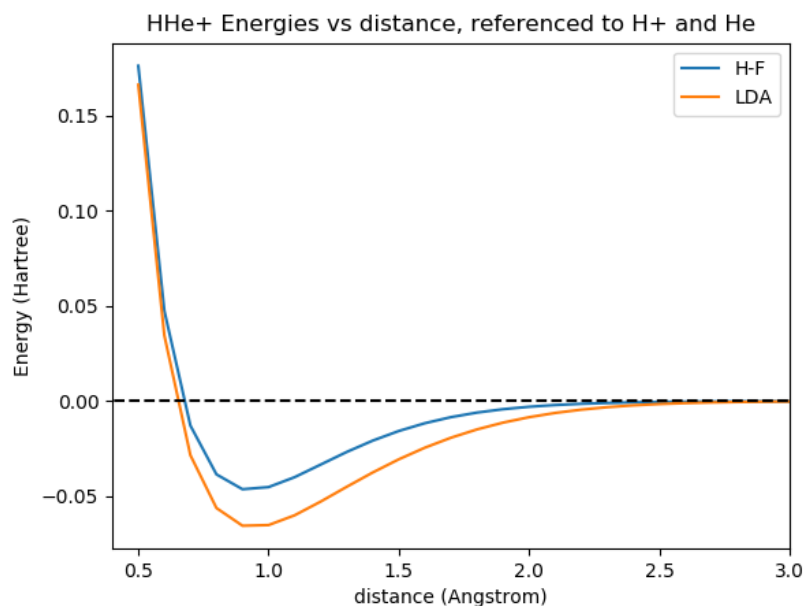

Equilibrium distance? How's the dissociation state? Bond energy? Truth is about -0.075 Hartree. LDA has advantage of cancellation of errors between exchange and correlation errors. A good thing!
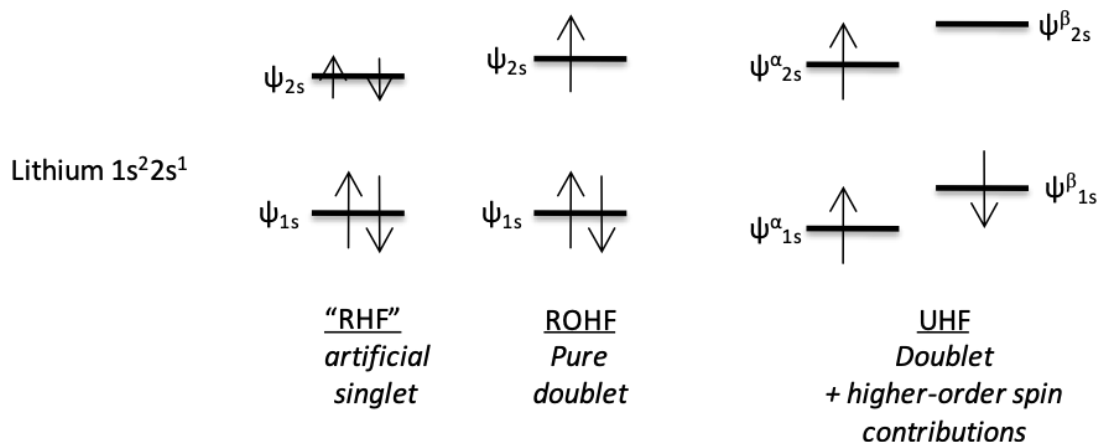
5.6.3 Dissociated He2 example
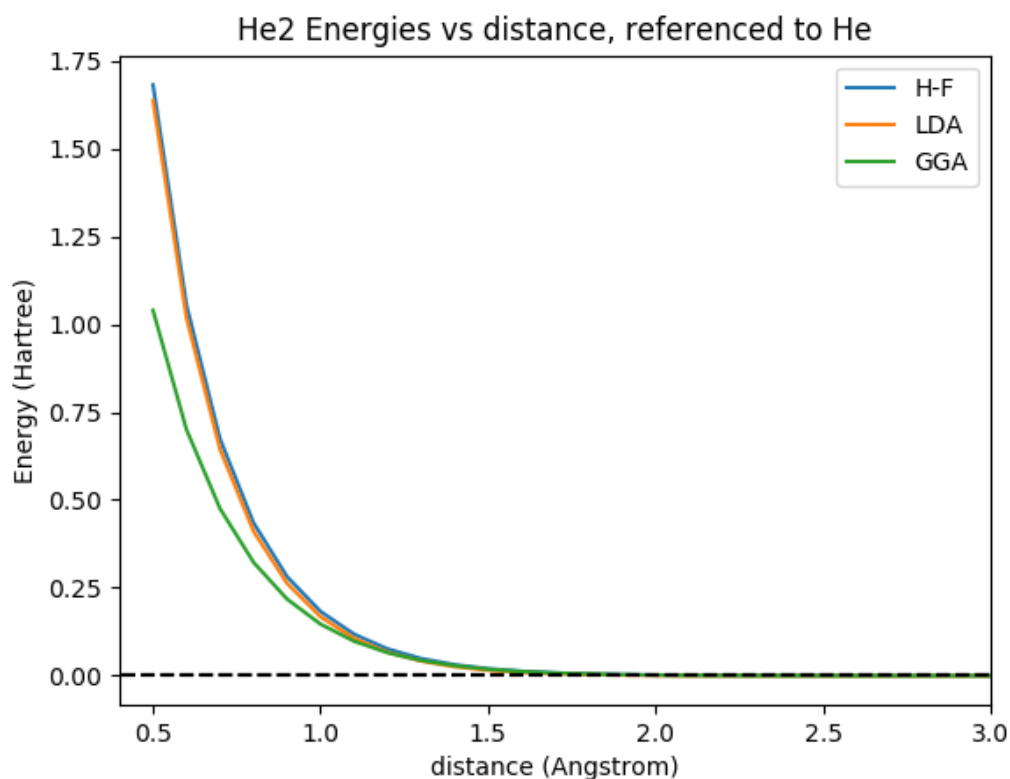
5.7 Open-shell systems

First, some jargon related to unpaired electrons:

# unpaired electrons	S	$2S+1$	name
0	0	1	singlet
1	1/2	2	doublet
2	1	3	triplet
3	3/2	4	quartet

Model has to be generalized somewhat to deal with systems with unpaired electrons. One approach is to construct wavefunctions that are exactly spin-adapted (eigenfunctions of the $\hat{S}$ operator). Possible in the Hartree-Fock world, but messy. More common is to relax that constraint a bit, define different orbital wavefunctions for spin-up and spin-down electrons, called *unrestricted* or *spin-polarized* (opposite of *non-spin-polarized*!). Means that electron density has different spin-up and spin-down parts.

Lithium $1s^2 2s^1$

"RHF"
artificial singlet

ROHF
Pure doublet

UHF
Doublet + higher-order spin contributions

Controlled in `GAMESS` using the `$CONTRL` group:

```
$CONTRL SCFTYP = RHF   non-spin-polarized, default
        SCFTYP = UHF   spin-polarized
        MULT   = 1 (default), 2,...  spin multiplicity = 1 + number of unpaired electrons
        ICHARG = 0 (default), 1,...  net charge
 $END
```

5.8 Gaussian basis sets

Gaussian functions $(e^{-\zeta |\mathbf{r}|^2})$ are the most popular choice for atom-centered basis sets. They do not efficiently represent molecular wavefunctions, but one- and two-electron integrals in WFT can be solved analytically over Gaussians.

Other choices, like Slater functions $(e^{-\zeta |\mathbf{r}|})$ are possible but require numerical quadrature.

Gaussian basis sets have to be created for any given atom and must be used consistently within a set of calculations.

- Primitive is a single Gaussian function, possibly multipled by a polynomial to look like *s*, *p*, ... Defined by an exponent ζ that determines how extensive (small ζ) or compact the function is.

- Contraction is a pre-set linear combination of several primitive Gaussians.

- Basis set is a predefined set of exponents and contraction coefficients appropriate for some specific atom.

5.8.1 Gaussian basis set nomenclature

- Minimal basis contains one contracted function for every atomic orbital. STO-3G is the poster child.

- Double zeta contains two contracted functions for every atomic orbital

- Split valence is more common, single zeta in core, double zete in valence, typical of Pople basis sets, eg "6-31G"

- Triple-split valence would be "6-311G"

- <u>Spherical</u> vs <u>Cartesian</u> determines whether a *d* function have 6 or 5 parts (the sixth of which is an *s*).

- <u>Polarization functions</u> are functions of one angular momentum greater than the highest angular momentum occupied states, eg *p* function for H, or *d* function for C. Important to capture the polarization of charge when atoms make molecules. Arcane nomenclature, eg 6-31G(d,p) or 6-31G**.

- <u>Diffuse functions</u> are small exponent functions to describe anions or loosely bound electrons. Again argane nomenclature, eg 6-31+G(d,p). Yech.

- <u>Correlation consistent</u> and <u>atomic natural orbital</u> are series of basis sets that are constructed to be efficient and to improve systematically.

- <u>Complete basis set</u> (CBS) limit is notion of extrapolating energies from a series of systematically improving basis sets. Very common in high accuracy calculations.

5.8.2   Standard basis sets in `GAMESS`

Specified in $BASIS group. Some common choices, in increasing level of sophistication:

Name	Type	Flags
	Pople type	**The most venerable and widely used**
STO-3G	Minimal	GBASIS=STO NGAUSS = 3
3-21G	Split valence	GBASIS=N21 NGAUSS=3
6-31G(d)	Split valence polarized	GBASIS=N31 NGAUSS =6 NDFUNC=1
6-311+G(d,p)	Triple-split valence	GBASIS=N311 NGAUSS=6 NDFUNC=1 NPFUNC=1
	polarized and augmented	DIFFSP=1
	Polarization-consistent	**Good for DFT**
PC0	Split valence	GBASIS=PCseg-0 ISPHER=1
PC1	Split valence polarized	GBASIS=PCseg-1 ISPHER=1
PC2	Triple split double polarized	GBASIS=PCseg-22 ISPHER=1
	Correlation-consistent	**Good for MP2 and beyond**
cc-pVDZ	Split valence polarized	GBASIS=CC2
cc-pVTZ	Triple split double polarized	GBASIS=CC3
aug-cc-pvDZ	augmented with diffuse functions	GBASIS=ACC2
	Effective core potentials	**Good for treating heavy atoms**
SBKJC	Split valence + core potential	GBASIS=SBKJC
Hay-Wadt	Split valence + core potential	GBASIS=HW

Complicated field, which is why the old standards live on in routine calculations. Optimal approach is to employ a <u>composite model</u>, calibrated by someone else, with well defined set of basis functions and treatments of exchange and correlation. A composite model pieces together results from a number of different calculations to estimate a higher accuracy model.

5.9 Electron cores

Low energy "core" electrons typically don't participate in chemical bonding but can add substantially to computational cost. Generally seek approximations, especially for heavy elements/metals.

Heart of approach is to partition an atom into core and valence parts. Seek ways to express the influence of the core on the valence without actually having to compute the core. Essentially seek to write

$$\hat{v}^{\text{ee}} \approx \hat{v}^{\text{ee,core}} + \hat{v}^{\text{ee,val}}$$

where the core potential is some simpler, composite expression of the influence of the core on the valence. Typically take the electron cores as "frozen" in the pure atomic states, and express influence on valence through angular-momentum-dependent operators parameterized against accurate atomic calculations. Goal is to recover valence wavefunctions with less effort.

5.9.1 Relativistic effects

Relativistic kinetic energy is relativistic total energy minus the rest energy:

$$T = \sqrt{p^2 c^2 + m_0^2 c^4} - m_0 c^2$$

Taylor expanding about $p^2 = 0$ gives the <u>first-order mass-velocity correction</u>:

$$T \approx \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3 c^2}$$

Reduces to non-relativistic result when $c \to \infty$. Electrons near core move at speeds close to c, second term becomes non-negligible and diminishes their energy. Most important for s states that penetrate closest to nucleus; they shield nucleus better and other valence states rise up in energy.

Electron spin and orbital magnetic moments also couple when $l > 0$, leads to <u>spin-orbit coupling</u> that splits p, d, ... states into $j = l \pm s$ states.

<u>Darwin correction</u> corrects s orbitals for electron and nucleus being at the same point; comes from solution of full Dirac relativistic equation for the atom.

Relativistic effects typically incorporated implicitly, by including in model for core electrons and thus capturing their effect on the valence. Spin-orbit, if necessary, added after the fact.

5.9.2 Implementations

Non-relativistic and relativistic effective core potentials (ECPs) available for many elements. These specify the potential felt by the valence electrons due to the core in terms of radial potential functions and angular projection operators. Typically these have to be combined with basis functions designed to work with them.

Most common are Hay-Wadt (LANL) and Stevens-Basch-Krause (SBK). Other more modern ones also available, like Stuttgart.

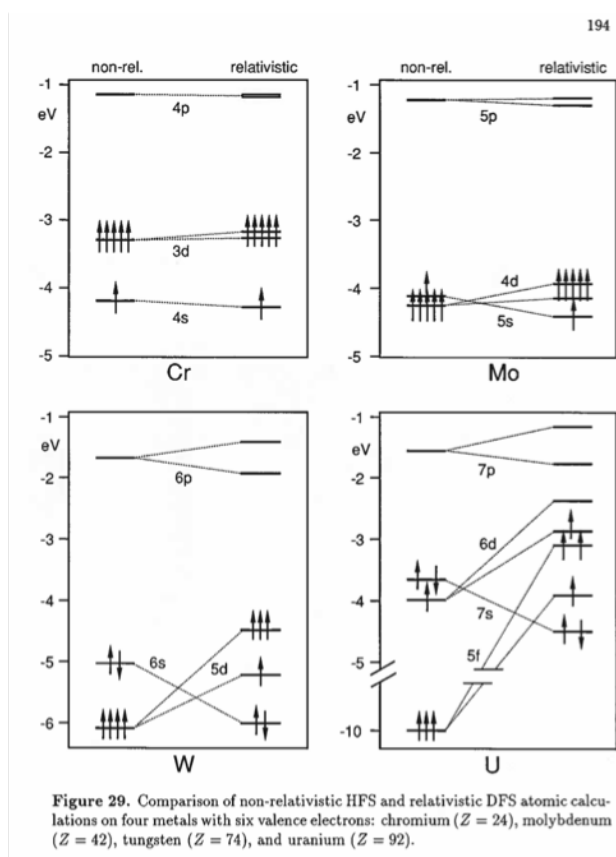Essential to all plane-wave codes, like `Vasp`, but implemented differently. Will touch on later in class.

Figure 29. Comparison of non-relativistic HFS and relativistic DFS atomic calculations on four metals with six valence electrons: chromium ($Z = 24$), molybdenum ($Z = 42$), tungsten ($Z = 74$), and uranium ($Z = 92$).

Figure 8: Comparison of Non-Relativistic and Relativistic Atomic States.

5.10 Population analysis

The molecular orbitals contain information that can be helpful in understanding structure and bonding:

- <u>Charge density</u> most direct representation of electron distribution

$$\rho(\boldsymbol{r}) = \sum_{\text{occupied}} |\psi_i(\boldsymbol{r})|^2 = \sum_{\mu,\nu} P_{\mu,\nu} \phi_\mu(\boldsymbol{r}) \phi_\nu(\boldsymbol{r})$$

- <u>Moments</u> of charge density (dipole, quadrupole), useful for thinking about molecule-molecule interactions. (Only exactly defined for neutrals!)

- <u>Electrostatic potential</u>, or Coulomb potential created by electrons and nuclei. More refined way of thinking about "how spots" on a molecule. Commonly used to parameterize classical forcefields, by seeking set of atom-centered charges that reproduce calculated electrostatic potential, as is done with `CHELPG`. Not uniquely defined.

- <u>Population analyses</u>, which attempt to distribute electrons to individual atoms and possibly bonds based on decomposition of molecular orbitals. Chemically it is intuitively nice to assign charge to individual atoms. There is no single "right" way to do this...the "charge" on an atom in a molecule in not uniquely defined! Consider an occupied molecular orbital ψ made up of two basis functions on two different atoms, α and β:

$$\begin{align} \psi &= c_\alpha \phi_\alpha + c_\beta \phi_\beta \tag{44} \\ \langle \psi | \psi \rangle &= c_\alpha^2 + c_\beta^2 + 2 c_\alpha c_\beta \langle \phi_\alpha | \phi_\beta \rangle \tag{45} \end{align}$$

In *Mulliken* analysis, c_α^2 is fraction of ψ assignable to the atom of α, c_β^2 fraction assigned to atom of β. Remainder is the "overlap" population, which is split evenly between the two. Summing over all occupied orbitals and subtracting nuclear charges gives *gross atomic charges*.

In *Löwdin* analysis, basis functions are pre-orthogonalized, so last term vanishes.

Both approaches very sensitive to choice of basis set. Only sensible to compare within a common model type across molecules.

- <u>Localized orbitals</u> is notion of creating linear combinations of ψ that satisfy some constraint for being compact. Leads to orbitals that are more naturally "bonding."

- <u>Natural orbitals</u> a rigorous scheme for orthogonalizing and assigning charge. Based on recognition that there is a set of orthogonal orbitals that optimally describe the density. Localizing these give *natural bonding orbitals*. See 06Weinhold.pdf.

- <u>Bader analysis</u> another method, based on a geometric analysis of the total charge density. Define See Bader, R. F. W. Atoms in Molecules: A Quantum Theory; Oxford University Press: Oxford, 1990.

5.11 Molecular orbital (MO) diagrams

Correlate molecular orbitals with their parent fragments. Use to be the thing. Seldom now

5.12   Implementation details of SCF methods

Basis is often *orthonormalized* to eliminate overlap from H-F-R equation; allows equations to be solved by matrix diagonalization.

Initial density matrix **P** are obtained by solving an approximate Hamiltonian (like extended Hückel). Always beware! Initial guess can influence final converged state.

Because the number of 2-electron integrals grows as N^4, they are sometimes calculated as needed "on-the-fly", so-called direct SCF.

Hartree-Fock integrals can be computed analytically in a Gaussian basis. Any other choice of basis, or any DFT functional, requires integrals to be computed by quadrature. Used to be a real hang-up. Today, algorithms are very robust to establish grids and do quadrature.

5.13   SCF updating

The SCF procedure is an optimization problem: find set of coefficients that minimizes the total energy. As discussed above, success depends on a reasonable initial guess for density matrix and judicious updating. Various strategies can be used to speed and stabilize convergence, like damped mixing of previous cycles.

Second-order SCF is a convergence acceleration method that requires calculation or estimation of the first- and second-derivatives of the energy with respect to the orbital coefficients. See e.g. Chaban et al., *Theor. Chem. Accts.* **1997**, *97*, 88-95.

Pulay's "direct inversion in the iterative subspace," or "DIIS," is a popular and powerful acceleration procedure that extrapolates from several previous Fock matrices to predict optimal next Fock to diagonalize. **An opportunity for machine learning?**

Controlled in GAMESS using the `$SCF` group.

```
$SCF DIRSCF=   .T./.F. controls direct scf
     SOSCF=    .T./.F. second-order scf
     DIIS=     .F./.T. direct inversion in the iterative subspace
     DAMP=     .T./.F. damping, on for initial iterations
$END
```

Can also control initial guess orbitals. Particularly powerful feature is to restart from converged orbitals from a previous calculations (.dat file), controlled with `$GUESS` group.
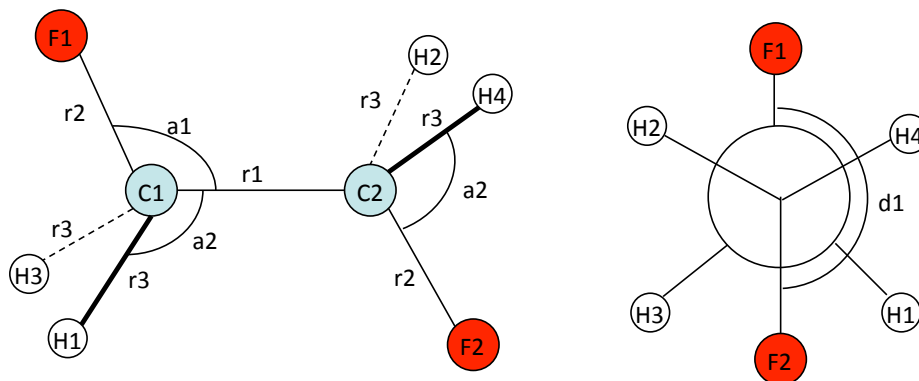
```
$GUESS GUESS = HUCKEL   construct intial guess from a simple Hamiltonian
             = MOREAD   read in orbitals from $VEC group.
```

6 Potential energy surfaces

The potential energy surface ("PES") is the sum of the repulsive energy of the nuclei and the kinetic and potential energies of all the electrons:

$$E_{\text{PES}}(\mathbf{R}_\alpha, \mathbf{R}_\beta, \dots) = E_{\text{elec}} + \sum_{\alpha=1}^{N} \sum_{\beta=\alpha+1}^{N} \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} \tag{46}$$

6.1 Specifying atomic positions

6.1.1 Cartesian

Computationally straightforward but don't correspond with our physical notion of bonds, bends, etc. Easiest to get out of a piece of software. A molecule has $3N - 6$ internal degrees of freedom ($3N - 5$ if linear), but Cartesians specify $3N$. The extra values correspond to the location of the center of mass and molecular oriendation. Codes will typically center and reorient the Cartesians.

In `GAMESS`, would specify Cartesian coordinates for FCH_2CH_2F like this:

```
 $CONTRL COORD=CART $END
 $DATA
FCH2CH2F drag calculation
C1
C      6.0     -3.76764     0.33879     0.03727
C      6.0     -2.35246     0.34495     0.03689
F      9.0     -4.72277     0.58147    -1.18012
F      9.0     -1.59909    -0.68487    -0.83662
H      1.0     -4.04387     1.08375     0.75395
H      1.0     -3.92958    -0.71060     0.16941
H      1.0     -2.03786     0.18875     1.04760
H      1.0     -2.09983     1.28759    -0.40187
 $END
```

6.1.2 Internal coordinates

These provide a more intuitive representation and can be convenient when building molecules by hand. In codes like `GAMESS`, most commonly defined using "z-matrix" notation. Specify each atom

in terms of its distance, angle, and dihedral angle with three previous atoms.

In Gamess, would specify z-matrix for FCH_2CH_2F like this:

```
$CONTRL SCFTYP=RHF RUNTYP=ENERGY COORD=ZMT $END
$DATA
FCH2CH2F drag calculation
C1
C
C   1   r1
F   2   r2   1   A1
H   2   r3   1   A2   3   D1
H   2   r4   1   A3   3   D2
F   1   r2   2   A1   3   D3
H   1   r3   2   A2   6   D1
H   1   r4   2   A3   6   D2

r1=1.5386
r2=1.39462
r3=1.11456
r4=1.12
A1=109.54214
A2=111.
A3=110.
D1=120.
D2=-120.5
D3=50.
$END
```
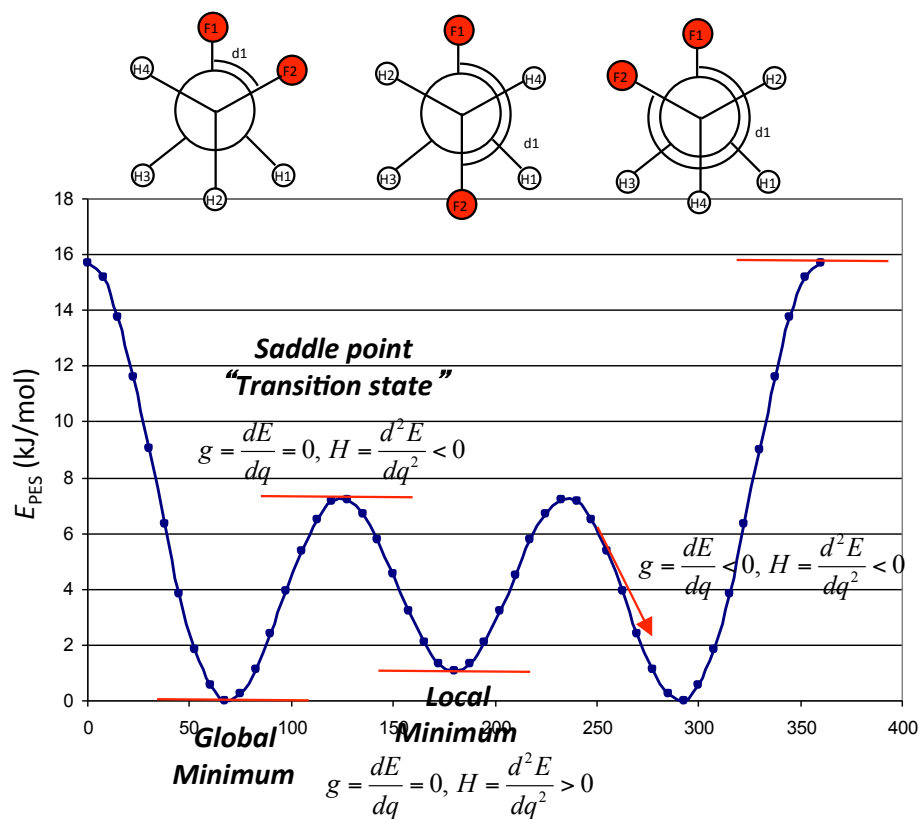
Particularly convenient when you'd like to "scan" over the value of some coordinate. Variable can be applied to more than one independent coordinate, if the molecule has symmetry.

6.2 Features of potential energy surfaces

6.2.1 One-dimensional example

Note 3-fold periodicity as expected for rotation about a CC single bond. Note too there are some special points:

- <u>Minima</u> are places where energy bottoms out. More formally, first derivative of energy, or slope, or "gradient" $g = 0$, and second derivative, or curvature, or "Hessian" $H > 0$. These are the **locally** stable conformations of the molecule. Note that lowest energy in this case is not trans, but rather gauche conformations. Are you surprised?

- <u>Saddle points</u> are places where energy is maximized. Physically, corresponds to "transition states" connecting low-energy conformations. Gradient $g = 0$, but curvature $H < 0$.

6.2.2 Many-dimensional PES features

Gradient becomes vector and Hessian a matrix

$$
\boldsymbol{g} = \begin{pmatrix} \frac{\partial E}{\partial q_1} \\ \vdots \\ \frac{\partial E}{\partial q_{3N}} \end{pmatrix} \qquad \boldsymbol{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial q_1^2} & \cdots & \frac{\partial^2 E}{\partial q_1 \partial q_{3N}} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial q_1 \partial q_{3N}} & \cdots & \frac{\partial^2 E}{\partial q_{3N}^2} \end{pmatrix}
$$

- <u>gradient</u> is vector tangent to PES. The force on an object is $\boldsymbol{F} = -\boldsymbol{g}$, so the gradients are often called the forces. Where gradient (slope) is negative, force is positive, and vice versa.
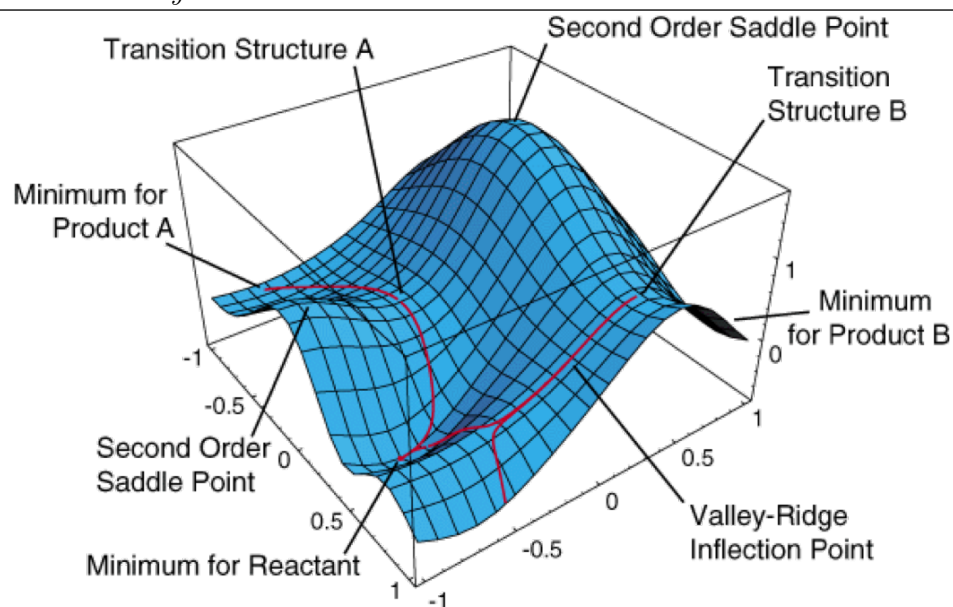
Figure 9: From Schlegel, *J. Comp. Chem.* **2003**, *24*, 1514-1527.

Force always pushes system toward nearest minimum. If the potential is harmonic, then the force constant $k = H$, so the Hessian is also called the "force constant."

- Hessian matrix is real and symmetric. Diagonalization gives eignevalues and eigenvectors. Eigenvectors give "natural" directions along PES (physically, the harmonic vibrational modes), and eigenvalues indicate curvature in that direction.

- Minimum on multidimensional PES has gradient vector $\boldsymbol{g} = 0$ and all positive Hessian eigenvalues.

- First-order saddle point, or transition state, has $\boldsymbol{g} = 0$ and one and only one negative Hessian eigenvalues. (Physically, one unique direction that leads downhill in energy.) Must correspond to lowest-energy point connecting two minima.

- Minimum energy pathway (MEP) or intrinsic reaction coordinate (IRC) is steepest descent pathway (in mass-weighted coordinates) from saddle point to nearby minima. Path a marble with infinite inertia would follow.

- Higher order saddle points have $\boldsymbol{g} = 0$ and more than one negative Hessian eigenvalue. Can always lead to lower energy first order saddle point. These generally do not have chemical significance.

In computational chemistry/materials science, it is frequently our job to identify the critical points (minima and transition states on a PES). In liquids, PES much more flat and lightly corrugated. Statistical mechanics becomes mores important.

Each distinct electronic state defines its own PES. Remember that there are multiple PES's for any atom configuration, corresponding to different electronic states. Sometimes these states can interact, intersect, giving avoided crossings, conical intersections. Lead to more complicated dynamical behavior.

6.3   Energy gradients and second derivatives

6.3.1   Gradients

$$\frac{\partial E_{\text{elec}}}{\partial q_i} = \frac{\partial}{\partial q_i}\langle\Psi|\hat{H}|\Psi\rangle = \langle\frac{\partial\Psi}{\partial q_i}|\hat{H}|\Psi\rangle + \langle\Psi|\frac{\partial\hat{H}}{\partial q_i}|\Psi\rangle + \langle\Psi|\hat{H}|\frac{\partial\Psi}{\partial q_i}\Psi\rangle$$

- Hellman-Feynmann theorem says that sum of first and last terms vanish, so in principle only need to compute middle, which involves derivative of Coulomb potential and can be evaluated.

- Pulay forces are forces from first and last terms that appear when basis functions are centered on atoms. An advantage of plane-wave basis sets, for which these terms vanish.

6.3.2   Hessian

In some electronic structure models can be computed analytically. More commonly, determined from numerical differentiation of gradients. Implementations typically assume that system is at minimum.
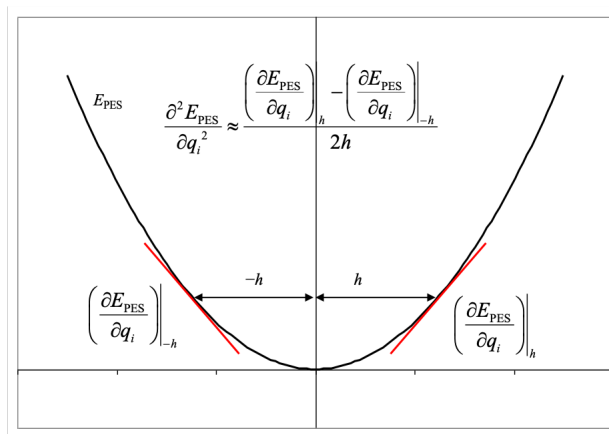
h must be small enough to stay in the harmonic region, but big enough to avoid numerical noise swamping the gradients.

For a molecule with N atoms, to construct complete $3N \times 3N$ Hessian, have to evaluate gradients $6N$ times for two-sided differencing. Each pair of displacements completes one row of Hessian. Obviously tends to be quite expensive.

To get better precision and accuracy, could calculate more than two displacements, and could fit to a more complicated function than a harmonic potential.

6.4   Geometry optimization algorithms

6.4.1   Energy-only

- Trudge infers gradient and locates minimum by wandering around

6.4.2   Energy + gradient

- Steepest descent, just march down hill. $\boldsymbol{R}' = \boldsymbol{R} - \lambda\boldsymbol{g}$. Safe, very inefficient near minimum. May do line search to adapt λ.

- Conjugate gradient is steepest descent plus orthogonalization to previous step. Safe, less very inefficient, common choice when far from minima.

6.4.3 Energy + gradient + higher order

- Quasi-Newton Raphson takes advantages of both first and second derivative information:

$$\boldsymbol{R}' = \boldsymbol{R} - \boldsymbol{H}^{-1}(\boldsymbol{R})\boldsymbol{g}(\boldsymbol{R})$$

Typically do not know Hessian and it is expensive to calculate. Make an initial guess, then update Hessian with gradient information from each geometry step. "Learning" PES as we go. Generally converges very rapidly near minima, where surface is not too anharmonic.

- Rational function optimization is similar in spirit, also constructs Hessian, but uses more sophisticated (than quadratic) guess form of PES to update positions.

- Direct inversion in the iterative subspace (DIIS) uses sizes of QNR steps as estimates of error and constructs new step from linear combination of previous that minimizes error inferred from previous steps:
$$\boldsymbol{err}(\boldsymbol{R}) = \sum_i c_i \boldsymbol{H}_i^{-1} \boldsymbol{g}_i$$

Generally very efficient in region of minimum. Algorithm can misbehave away from minima, possibly even converging to nearby saddle points, so often started with conjugate gradient steps.

6.4.4 Machine learning

All of these based on some form of assumed model of underlying PES (Taylor expand to second order around minimum). Emerging are methods that "fingerprint" structure and construct and improve energy model with each step. Remains to be seen if a new "standard" emerges.

6.4.5 Global optimizations

Simulated annealling, genetic algorithms, ..., more on the exotic side.

6.4.6 Convergence criteria

Typically determine convergence by enforcing maximum on each individual force component

`GAMESS` offers a limited set of algorithms.

```
$STATPT METHOD = NR     ! Quasi-Newton Raphson
              = RFO    ! rational function optimization
        OPTTOL = 0.0001 ! convergence criterion in au/bohr.
        HESS = GUESS    ! guess an initial Hessian
             = READ     ! read from $VIB group
 $END
```

6.5   Specify `GAMESS` calculation type

Specified in $CONTRL group by RUNTYP flag:

Calculation	RUNTYP=
Single-point energy	Energy
Single-point energy + force	Gradient
Geometry optimization	Optimize
Linear scan over PES	Scan
Energy + second derivative	Hessian
Transition state search	Sadpoint
Intrinisc reaction coordinate	IRC

Note too that specifying EXETYP=CHECK will check your input without actually running the job.

Hessian (force) calculation can be done analytically or by numerical differentiation of forces, depending on electronic structure method:

```
$FORCE METHOD = ANALYTICAL
             = SEMINUM
       VIBSIZ = 0.01    ! step size (bohr)
$END
```

6.6   Efficient coordinate systems

Optimizations are most efficient in coordinate system that diagonalizes Hessian, so that optimizations along each direction are (nearly) independent. Large off-diagonal Hessian terms imply strong coupling. Cartesian coordinates do not reflect physical forces in system and are generally poor choice/slow convergence for optimizations. Can choose other coordinate systems. Forces/Hessian always computed in cartesians, so any other coordinate system requires transformations back and forth.

- Cartesians simplest to implement, consistent performance. Typically only choice in supercell calculations.

- Z-matrix are easy to define and use for organic molecules with no rings. For $3N - 6$ degrees of freedom, must specify $N - 1$ distances, $N - 2$ angles, and $N - 3$ dihedrals. Typically will converge much faster than Cartesians for small molecules. Implemented in most molecular codes, including `GAMESS`.

```
$CONTRL COORD=ZMAT NZVAR = 3N-6 $END
```

- Natural internals are generalizations of z-matrix that are coordinates that approximately diagonalize Hessian. Hard to generate *a priori* or automatically. Specification in `GAMESS` is arcane, done in `$ZMAT`.

- Redundant internals are an over-determined set of internal coordinates, like all bond distance, all angles between bonded atoms, all dihedrals. Easily constructed automatically. Mapping between Cartesians and redundant internals becomes more complicated; transform from redundant to Cartesians is overdetermined and has to be solved iteratively. Works very efficiently for molecules though. Implemented (in spirit) in `GAMESS`.

```
$CONTRL NZVAR = 3N-6 $END
$ZMAT DLC=.TRUE.  AUTO=.TRUE. $END
```

	FCH2CH2F	C5H10
Cartesian	13	30
Z-matrix	11	failed
Redundant/DLC	16	failed

6.7 Performance of models for geometries

Generally pretty good! Gross geometries of molecules can be computed with good reliability using common approximations (H-F, LDA, GGA). Subtler things (does FCH_2CH_2F really prefer *trans* or *gauche*?) can take more care in choice of electronic structure model. https://cccbdb.nist.gov/ is a great place to look for benchmarks.

6.8 Vibrational frequencies

Suppose we are at a minimum on a PES. Near that minimum, we can Taylor expand the PES and truncate at second order ("harmonic", or quadratic, approximation). The Schrödinder equation describing the dynamical motion of the nuclei can be written in terms of displacements from the equilibrium position, $q_i = x_i - x_i^{eq}$, $i = 1, \ldots, 3N$ and the Hessian H:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \frac{\partial^2}{dq_i^2} + \frac{1}{2} \sum_{i,j} H_{ij} q_i q_j$$

or in mass-weighted coordinates, $\xi_i = \sqrt{m_i} q_i$:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{\partial^2}{d\xi_i^2} + \frac{1}{2} \sum_{i,j} \tilde{H}_{ij} \xi_i \xi_j, \qquad \tilde{H}_{ij} = \frac{1}{\sqrt{m_i m_j}} H_{ij}$$

From eigenvalues κ_i and eignevectors s_i ("normal modes") of mass-weighted Hessian, can transform into $3N$ one-dimensional problems:

$$\hat{H}_i = -\frac{\hbar^2}{2} \frac{d^2}{ds_i^2} + \kappa_i s_i^2$$

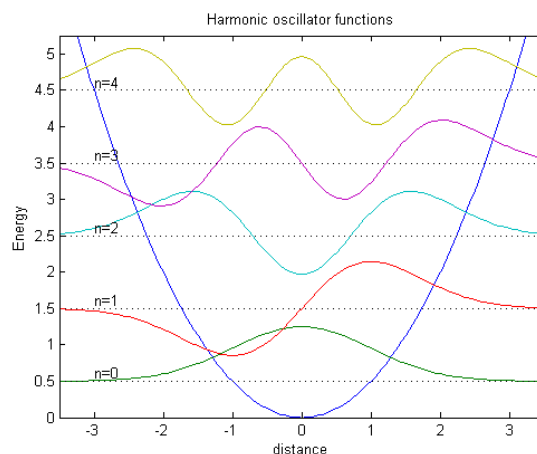This is one-dimensional harmonic oscillator Hamiltonian, solutions well known.

Table 4: Harmonic oscillator model

$$V(x) = \frac{1}{2}\kappa x^2, -\infty < x < \infty$$

$$\psi_v(x) = N_v H_v(x/\alpha) e^{-x^2/2\alpha^2}, v = 0, 1, 2, \dots$$

$$\alpha = (\hbar^2/\kappa)^{1/4}, N_v = (2^v v! \alpha \sqrt{\pi})^{-1/2}$$

Hermite polynomials
$$H_0(y) = 1$$
$$H_1(y) = 2y$$
$$H_2(y) = 4y^2 - 2$$
$$H_{n+1}(y) = 2y H_n(y) - 2n H_{n-1}(y)$$

$$\nu = \frac{1}{2\pi}\sqrt{\kappa}$$
$$E_v = \left(v + \frac{1}{2}\right) h\nu, v = 0, 1, 2, \dots$$

Do this in $3N$ Cartesian space, so 6 (or 5) of the normal modes correspond to translations and rotations of the molecule. If calculation is exact, these will have $\kappa_i = 0$. Numerical errors may make them somewhat non-zero. If necessary, these can be projected out by transforming Hessian to internal and back to Cartesian coordinates.

Note it is impossible for molecule to just sit at $q = 0$. Nuclei are *always vibrating* about x^{eq}. Gives zero point energy

$$ZPE = \frac{1}{2}\sum_i h\nu_i$$

For a chemical bond, $\kappa \approx 500\,\mathrm{N\,m^{-1}}$, $h\nu \approx 0.8\,\mathrm{eV}$.

6.8.1   Absorption intensities

Vibrational modes can be probed/observed spectroscopically. Intensity of stimulated absorption from vibrational state i to f given by Einstein coefficient of stimulated absorption:

$$B_{if} = \frac{|\mu_{if}|^2}{6\epsilon_0 \hbar^2}$$

Arises from coupling of electric field of light with dipole of system. Transition dipole moment, $\mu_{if})$ *givenby* $: \mu_{if} = \langle\psi_i|\hat{\mu}|\psi_f\rangle$ where $\hat{\mu}$ is dipole operator,

$$\hat{\mu} = \sum q_i \boldsymbol{r}_i$$

where sum runs over all charged particles and q_i is each charge. Dipole moment changes as molecule vibrates. In direction ξ, can write

$$\hat{\mu}(\xi(t)) = \mu(0) + \xi(t)\left(\frac{d\mu}{d\xi}\right)_{\xi=0} + \dots$$

Use harmonic oscillator wavefunctions for ψ_i and ψ_f:

$$\mu_{if} = \langle\psi_i|\hat{\mu}|\psi_f\rangle = \langle\psi_i|\mu(0)|\psi_f\rangle + \left(\frac{d\mu}{d\xi}\right)_{\xi=0}\langle\psi_i|\xi|\psi_f\rangle + \ldots$$

First integral vanishes for $i \neq f$. Second integral provides *gross selection rule* that intensity of transition proportional to the *dynamic* dipole moment along vibrational normal mode ξ and *particular selection rule* that intensity of transition is zero unless $f = i \pm 1$. Latter comes from nature of Hermite polynomials. At normal temperatures, $i = 0$, and the only observable vibrational transitions are $1 \rightarrow 2$.

6.8.2   Performance of harmonic approximation for vibrational spectrum

Harmonic vibrational frequency systematically overestimate experiment. Convolution of *harmonic approximation* error: actual PES is not exactly harmonic, and errors intrinsic to electronic structure model. Errors are typically systematic (see eg https://doi.org/10.1021/jp960976r).

	scale factor
HF/3-21G	0.9085
HF/6-31G(d)	0.8929
MP2/6-31G(d)	0.9434
B3LYP/6-31G(d)	0.9613

Relative intensities are generally predicted with good reliability. Model predicts absorption peaks to be delta functions. Peaks always broadened due to a variety of fundamental and instrumental considerations. Common in displaying spectra to arbitrarily broaden using a Lorentzian function.
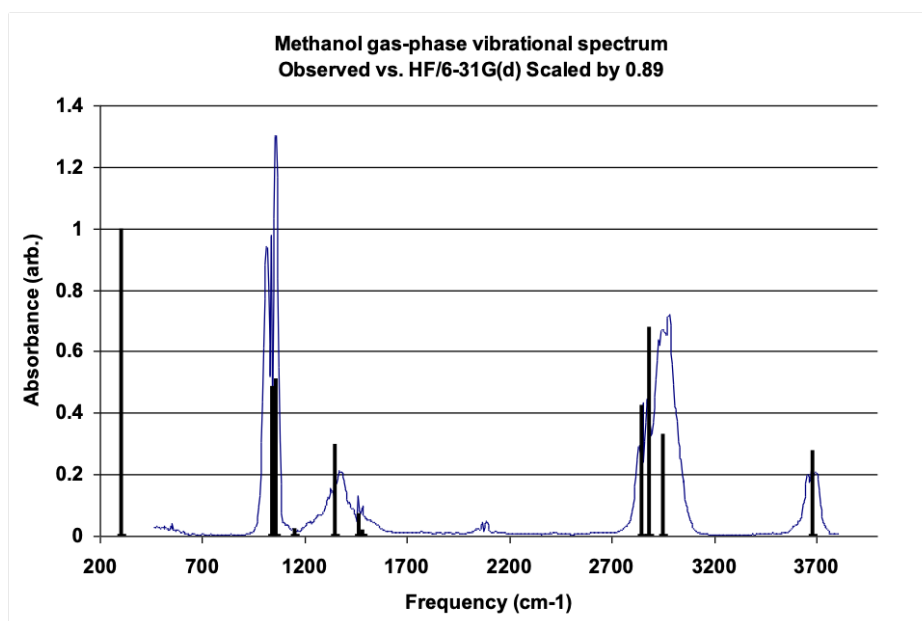

**Figure 10:** Scaled HF/6-31G(d) vibrational spectrum vs experiment

6.9 Transition states

6.9.1 Symmetry

Can exploit symmetry to force calculation to converge to a transition state. Eclipsed form of FCH_2-CH_2F has mirror symmetry (C_s), if initialized in that configuration, optimization must preserve symmetry.
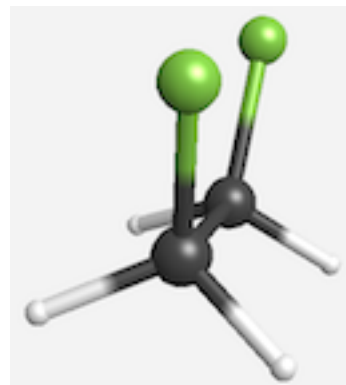
```
 $DATA
  FCH2CH2F eclipsed z-matrix (Cs, or mirror, symmetry)
CS

 C
 C       1   1.5000000
 F       2   1.4000000  1   109.5421400
 H       2   1.1000000  1   109.5421400  3   120.0000000  0
 H       2   1.1000000  1   109.5421400  3  -120.0000000  0
 F       1   1.5000000  2   109.5421400  3     0.0000000  0
 H       1   1.1000000  2   109.5421400  6   120.0000000  0
 H       1   1.1000000  2   109.5421400  6  -120.0000000  0
 $END
```

See results in `../Labs/Gamess/FCH2CH2F/SYMMETRY`.
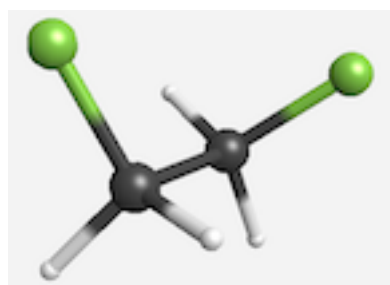
$-277.937\,777\,074\,9\,\text{au}$ $\longrightarrow$ $-277.925\,347\,844\,1\,\text{au}$

$$\Delta E = 0.34\,\text{eV}$$

6.9.2 Coordinate drag

If reaction state coordinate maps closely onto some internal coordinate, then can do a series of "constrained" optimizations, fixing the coordinate of interest to a series of values and relaxing all other coordinates. Use `IFREEZ` within `GAMESS`. For example, define FCH_2CH_2F using z-matrix and freeze $F-C-C-F$ dihedral angle at a series of values.

```
 $CONTRL SCFTYP=RHF DFTTYP=PBE RUNTYP=OPTIMIZE COORD=ZMT NZVAR=18 ISPHER=1 $END
 $BASIS GBASIS=PCseg-1 $END
 $STATPT IFREEZ(1)=12 $END
 $DATA
FCH2CH2F eclipsed TS
C1
```

```
C
C   1   r1
F   2   r2   1   A1
H   2   r3   1   A2   3   D1
H   2   r4   1   A3   3   D2
F   1   r5   2   A4   3   D3
H   1   r6   2   A5   6   D4
H   1   r7   2   A6   6   D5


...
D4=120.

...
 $END
```

See results in ../Labs/Gamess/FCH2CH2F/SCAN.
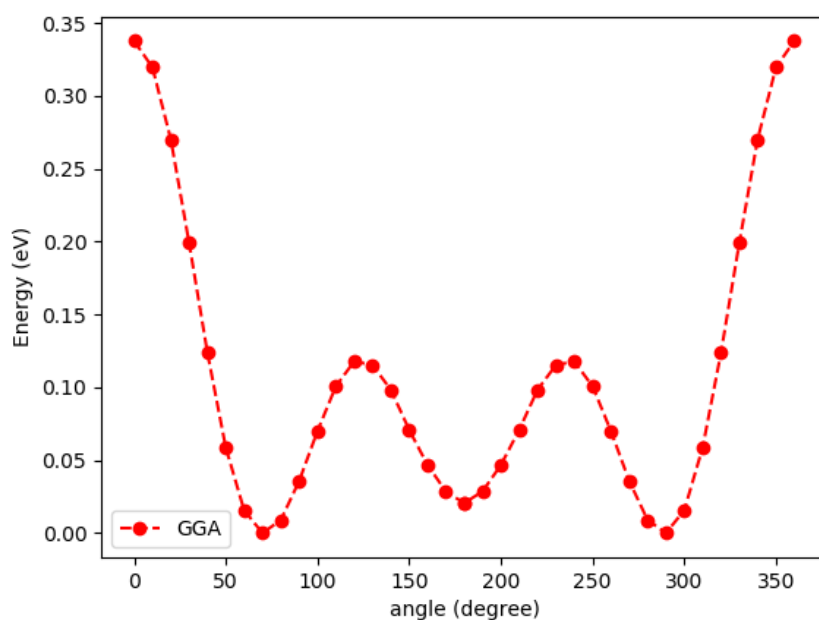

Figure 11: GGA/PCseg-1 rotational scan

A quasi-NR optimization started at one of the approximate TS's will usually converge to the exact TS.
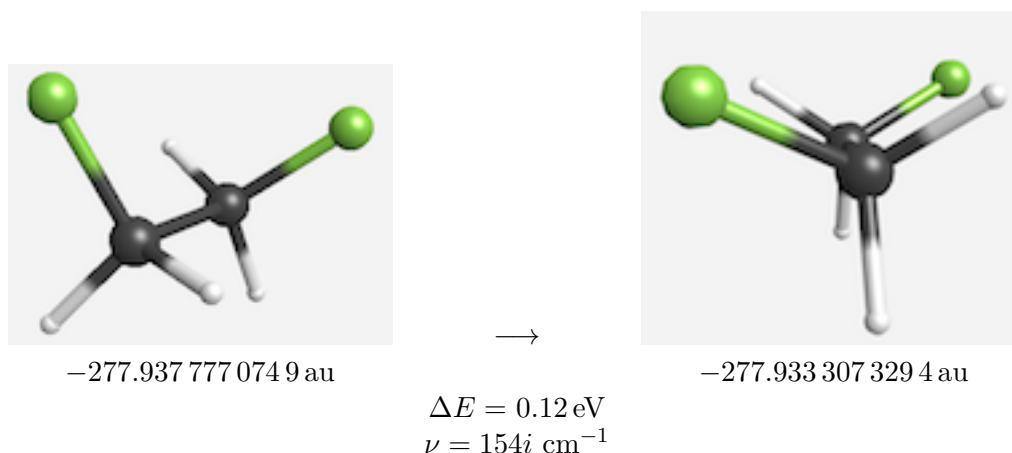
```
 $CONTRL SCFTYP=RHF DFTTYP=PBE RUNTYP=OPTIMIZE COORD=ZMT NZVAR=18 ISPHER=1 $END
 $STATPT METHOD=NR $END
 $BASIS GBASIS=PCseg-1 $END
 $DATA
FCH2CH2F zmatrix optimization near saddle point, no hessian
C1
 C
 C     1   1.5256029
```

```
F      2   1.4018052  1   110.3919125
H      2   1.1066523  1   112.5759655  3   119.5903058  0
H      2   1.1070172  1   108.5521191  3  -119.1579857  0
F      1   1.4018888  2   110.3079213  3   120.0000000  0
H      1   1.1065092  2   112.5372024  6   119.5247291  0
H      1   1.1069911  2   108.5976341  6  -119.1645584  0
$END
```

See results in ../Labs/Gamess/FCH2CH2F/QNR-TS. Always good practice to follow up with a frequency calculation to confirm.

$-277.937\,777\,074\,9\,\mathrm{au}$

$\longrightarrow$

$-277.933\,307\,329\,4\,\mathrm{au}$

$$\Delta E = 0.12\,\mathrm{eV}$$
$$\nu = 154i\ \mathrm{cm^{-1}}$$

Coordinate dragging can fail when the reaction coordinate is non-linearly related to the multiple internal coordinates. Plus, it is relatively expensive, as it involves a lot of optimizations.

6.9.3   1st order methods (NEB, ...)

A scan is a first order method that freezes the gradient along a search direction. A better algorithm would use the information along the search direction to find the TS and the entire MEP. That's the spirit of a *nudged elastic band* calculation, for instance. Also of newer methods to generate more sophisticated approximations. Touch on that later....

6.9.4   2nd order methods

Hessian-based methods (like quasi-NR and DIIS) generally work more efficiently, assuming you can find a region reasonably close to the TS and can get a good guess of the Hessian with the appropriate (1!) number of negative eigenvalues. These work like regular optimization methods, but search uphill along the negative eigenvector and downhill along the other directions. The Hessian update scheme has to be appropriately modified to accommodate the negative eigenvalue. The choice of coordinate system can become even more crucial.

Algorithm:

1. Identify and optimize structures of reactant and product states

2. Guess a structure for the TS, interpolated either mathematically or empirically between reactant and product

3. Compute initial TS Hessian. Only needs to be approximately correct, so appropriate to use a less-expensive method.

4. Confirm Hessian has desired form.

5. Do saddle-point search with guessed Hessian

6. Check result with final Hessian calculation

```
$CONTRL SCFTYP=RHF DFTTYP=PBE RUNTYP=SADPOINT COORD=CART ISPHER=1 $END
$BASIS GBASIS=PCseg-1 $END
$FORCE HESS=READ $END
$DATA
H2ON2
C1        1
N         7.0      0.9405942384     -0.3241591975     -0.0156283505
N         7.0      0.0107640781      0.6540868381      0.0152029180
O         8.0     -0.9317086136     -0.2406652788     -0.0189127039
H         1.0     -0.2853795803     -0.9336844866      0.3015543918
H         1.0      1.8537652825      0.1690870887      0.0045149723
 $END
 $HESS
ENERGY IS     -184.6737814637 E(NUC) IS       74.1740447013
 1  1 8.31017204E-01 1.46125961E-01 7.06555414E-04-1.42105871E-01 2.88851646E-02
 1  2-1.06097190E-03-3.64083936E-01 2.22079857E-02-2.60487424E-03-3.19838288E-02
.....
 $END
```

6.9.5 Well climbing

Algorithms exist that will climb out of basins and seek transition states. . . .

6.10 Intrinsic reaction coordinates

6.11 Molecular dynamics

Basic idea is to propogate atoms forward in time using some model to compute the forces on atoms and Newton's laws to describe kinetic energy of atoms. May be done at constant energy (NVE) or, by coupling kinetic energy to an appropriate reservoir, at constant temperature (NVT). Details beyond this course (perhaps beyond this instructor!). Primary point for us is that cost of electronic structure calculations is great enough that typically some adjustments must be made to make force calculations cheap and fast enough to support number of evaluations necessary to do meaningful dynamics.

6.11.1 Cheap parameters

Simplest trick is to back off on the precision and accuracy of calculations to reduce force evaluation cost.

6.11.2 Car-Parrinello dynamics

Treat wavefunction itself as a dynamical variable and propogate forward in time along with the nuclei. Ideally parallels but does not exactly follow Born-Oppenheimer energy surface. Huge advance when originally introduced, has fallen out of favor as more conventional B-O approaches compete more effectively.

6.12 Biased sampling

7 First-principles thermodynamics

7.1 Connection Between QM and Thermodynamics

We have focused to this point on the many approaches and details of calculating the *internal electronic energy* of a single molecule, that is, the energy associated with taking infinitely separated constituent nuclei and electrons at rest and forming a molecule:

$$2\ H^+ + 8\ O^{8+} + 10\ e^- \rightarrow H_2O \qquad E^{elec} \tag{47}$$

E^{elec} is typically calculated within the Born-Oppenheimer approximation, i.e.\ within the approximation that the nuclei are fixed in space at the minimum energy configuration. Even at 0~K, by quantum mechanics the atoms must vibrate about this minimum, and this intrinsic vibration imparts a *zero-point vibrational energy* (ZPVE) to the molecule, and the 0~K internal energy of a molecule is thus:

$$E^0 = E^{elec} + ZPVE \tag{48}$$

ZPVE can be calculated reliably within the harmonic approximation, according to

$$\text{ZPVE} = \frac{1}{2}h\sum_{i=1}^{3n-6}\nu_i \tag{49}$$

where ν_i are the harmonic vibrational frequencies, obtained from a vibrational frequency analysis. E^0 is the minimum physically meaninfful energy of the molecule.

Energy can be deposited in a molecule in many other ways as well, e.g.\ as translational and rotational kinetic energy, in excited vibrational modes, in the interaction of a molecule with an external electric or magnetic or gravitational field, or .... If we assume that the energy in these various degrees of freedom are separable, we can write:

$$E_i = E^0 + E^{trans} + E^{rot} + E^{vib} + E^{elec*} + E^{ext} \tag{50}$$

To fully describe microscopic energetic state of a molecule, would have to specify all of these.

Typically, though, we are more interested in the collective properties of many molecules at equilibrium, like the internal energy U or enthalpy H or Gibbs energy G, under some external constraints like temperature T or volu me V. These thermodynamic quantities are averages over the energy states of an *ensemble* of molecules. The way this averaging is performed is the realm of *statistical thermodynamics.*

Most important for us will be the *canonical ensemble*, in which the free variables are the number of molecules N, the total volume V, and the temperature T. Offer without proof, in the canonical ensemble the probability for a molecule to be in some energy state E_i above E^0 is given by the Boltzmann factor,

$$P(E_i) \propto e^{-E_i\beta} = e^{-E_i/k_BT}, \qquad \beta = 1/k_BT \tag{51}$$

Defines an exponentially decaying probability function for a state to be occupied at some temperature. In a sense, *temperature* is the property of a system following this distribution.
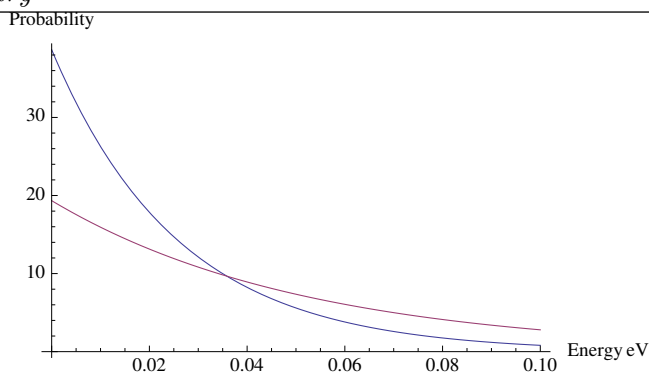
Figure 12: Boltzmann distribution at two different temperatures

7.1.1 Averages and partition functions

Let's use this to calculate the internal energy U of a molecule at some temperature.

$$U(T) = \frac{\sum_i E_i P(E_i)}{\sum_i P(E_i)} \tag{52}$$

where the denominator ensures that the probability is normalized.

$$U(T) = \frac{\sum_i E_i e^{-E_i \beta}}{\sum_i e^{-E_i \beta}} \tag{53}$$

$$= \frac{\frac{\partial}{\partial \beta} \sum_i e^{-E_i \beta}}{\sum_i e^{-E_i \beta}} \tag{54}$$

$$= -\frac{\partial \ln \sum_i e^{-E_i \beta}}{\partial \beta} \tag{55}$$

The sum over energy states is evidently a special quantity, called the partition function:

$$q = \sum_i e^{-E_i \beta} \tag{56}$$

All thermodynamic quantities can be written in terms of the partition function!

7.1.2 Harmonic oscillator example

Harmonic oscillator is a reasonable model of a molecular vibration. Energy spectrum given by

$$E_v = (v + 1/2)h\nu, \qquad v = 0, 1, 2, ... \tag{57}$$

Let's define the energy qunatum $h\nu = \epsilon_0$ and reset the energy scale so that zero is at $1/2h\nu$:

$$E_v = v\epsilon_0, \qquad v = 0, 1, 2, ... \tag{58}$$

$$q(T) = \sum_{v=0}^{\infty} e^{-v\epsilon_0 \beta} \tag{59}$$

$$= \frac{1}{1 - e^{-\epsilon_0 \beta}} \tag{60}$$

where we take advantage of the fact that the sum is a geometric series to evaluate it in closed form.

Plot partition function vs T, increasing function.

Internal energy:

$$U(T) \quad = \quad -\frac{\partial \ln q}{\partial \beta} \tag{61}$$

$$= \quad \frac{\epsilon_0}{e^{\epsilon_0 \beta} - 1} \tag{62}$$

Heat capacity:

Entropy

7.2   Molecular Ideal Gas

Nice example above for a simple model. To get thermodynamics of an ideal gas, in principle need to sum over all the types of energy states (translational, rotational, vibrational, ...) of every molecule. Seemingly impossible task. One simplification is if we can write energy as sum of energies of individual elements (molecules) of system:

$$E_j = \epsilon_j(1) + \epsilon_j(2) + ... + \epsilon_j(N) \tag{63}$$

$$Q(N,V,T) = \sum_j e^{-E_j \beta} \tag{64}$$

$$= \sum_j e^{-(\epsilon_j(1) + \epsilon_j(2) + ... + \epsilon_j(N))\beta} \tag{65}$$

If molecules/elements of system can be distinguished from each other (like atoms in a fixed lattice), expression can be factored:

$$Q(N,V,T) = \left(\sum_j e^{-\epsilon_j(1)\beta} \right) \cdots \left(\sum_j e^{-\epsilon_j(N)\beta} \right) \tag{66}$$

$$= q(1) \cdots q(N) \tag{67}$$

Assuming all the elements are the same: $\tag{68}$

$$= q^N \tag{69}$$

If not distinguishable (like molecules in a liquid or gas, or electrons in a solid), problem is difficult, because identical arrangements of energy amongst elements should only be counted once. Approximate solution, good almost all the time:

$$Q(N,V,T) = q^N / N! \tag{70}$$

Sidebar: "Correct" factoring depends on whether individual elements are fermions or bosons, leads to funny things like superconductivity and superfluidity.

This $q(V,T)$ is the *molecular partition function*, and is calculated by summing over the individual energy states of a single molecule (starting at E_0).

Further simplified by factoring into contributions from various ($3N$) molecular degrees of freedom:

$$q(V,T) \quad = \quad \left(\sum_{\text{trans}} e^{-e_{\text{trans}}\beta} \right) \left(\sum_{\text{rot}} e^{-e_{\text{rot}}\beta} \right) \left(\sum_{\text{vib}} e^{-e_{\text{vib}}\beta} \right) \left(\sum_{\text{elec}} e^{-e_{\text{elec}}\beta} \right) \tag{71}$$

$$= \quad q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \tag{72}$$

$$U \quad = \quad E_0 + U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}} \tag{73}$$

Similarly for other thermodynamic quantities, for example,

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = C_{v,\text{trans}} + C_{v,\text{rot}} + C_{v,\text{vib}} + C_{v,\text{elec}} \tag{74}$$

Thermodynamic quantities are sums of contributions from indvidual degrees of freedom.

Have to somehow *model* these motions and have to use our quantum mechanical results to parameterize the models.

7.2.1 Translational partition function

Need a model molecules freely translating about in a box. How about the *particle in a box*?

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, \qquad n = 1, 2, 3, ... \tag{75}$$

Have to construct partition function for one molecule. For gas molecules at normal conditions, energy spacing is tiny. Spare the details, but find that q_{trans} can be written in terms of a *thermal wavelength* Λ:

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \tag{76}$$

$$q_{\text{trans}} = \frac{V^\circ}{\Lambda^3} \tag{77}$$

Λ depends only a molecule mass (that's easy!) and is of the order the box dimensions at which quantization is evident. Typically a tiny number (e.g. 1.7×10^{-11}~m for Ar in a 1 liter volume at 298 K. q_{trans} is, on the other hand, enormous: lots of translational freedom. V° defines the standard state volume.

Given this, can find all translational contributions to thermodynamics. S_{trans} gives the Sackur-Tetrode equation, the absolute entropy of a monatomic gas:

7.2.2 Rotational partition function

Model molecule as a rigidly rotating body. Body has three orthogonal moments of inertia I determined by the molecular structure.

7.2.3 Vibrational partition function

See harmonic oscillator above

7.2.4 Electronic partition function

Governed by Fermi-Dirac distribution Electronic degeneracy

7.3 CO T-dependent thermo example

8   GAMESS Cheat Sheet

8.1   Specifying electronic configuration

8.1.1   Closed shell (default)

```
$CONTRL RHFTYP=RHF MULT=1 $END
```

8.1.2   Open-shell (n = spin-multiplicity = # unpaired electrons + 1)

```
$CONTRL RHFTYP=UHF MULT=n $END
```

8.2   Specifying electronic structure method

8.2.1   Hartree-Fock (default)

8.2.2   DFT

```
$CONTRL DFTTYP=xxx $END
```

`Gamess` supports <u>many</u> DFT functionals. See the $DFT section of the manual for a full set. Common DFT methods include:

method	xxx
Slater	Slater
Local density approx	SVN
Generalized gradient approx	PBE
Hybrid DFT	B3LYP
"Minnesota" optimized	M06
	M11

8.3   Specifying geometry

Again `GAMESS` has a number of options, several of which are arcane and seldom used. Most common are Cartesian and z-matrix. Here I give examples ignoring any symmetry the molecule might have.

8.3.1   Cartesian

Specify an atom name, atomic number, and cartesian positions in Å. Over-specified, so code will typically center and reorient. Following is for gauche difluoroethane, FCH_2CH_2F.

```
$CONTRL COORD=CART $END
$DATA
FCH2CH2F drag calculation
C1
C    6.0    -3.76764     0.33879     0.03727
C    6.0    -2.35246     0.34495     0.03689
F    9.0    -4.72277     0.58147    -1.18012
F    9.0    -1.59909    -0.68487    -0.83662
H    1.0    -4.04387     1.08375     0.75395
H    1.0    -3.92958    -0.71060     0.16941
H    1.0    -2.03786     0.18875     1.04760
H    1.0    -2.09983     1.28759    -0.40187
```

```
$END
```

8.3.2 Z-matrix

Specify atom name, number of atom it is connected to, distance to that atom, number of atom it makes an angle with, value of the angle, number of the atom it makes a dihedral with, and value of the dihedral angle. Values may be given directly or as variables, followed by list of variable specifications. In `Gamess`, would specify z-matrix for FCH_2CH_2F like this:

```
$CONTRL COORD=ZMT $END
$DATA
FCH2CH2F drag calculation
C1
C
C   1   r1
F   2   r2   1   A1
H   2   r3   1   A2   3   D1
H   2   r4   1   A3   3   D2
F   1   r2   2   A1   3   D3
H   1   r3   2   A2   6   D1
H   1   r4   2   A3   6   D2

r1=1.5386
r2=1.39462
r3=1.11456
r4=1.12
A1=109.54214
A2=111.
A3=110.
D1=120.
D2=-120.5
D3=50.
$END
```

Particularly convenient when you'd like to "scan" over the value of some coordinate. Variable can be applied to more than one independent coordinate, if the molecule has symmetry. In general, though, variables should not be reused.

8.4 Geometry optimization coordinate system

By default, `GAMESS` performs optimizations in Cartesian coordinates.

To use z-matrix coordinates, specify

```
 $CONTRL COORDS=ZMT NZVAR=xx $END
```

where NZVAR = 3N-6.

To have `Gamess` automatically create a set of appropriate "delocalized" internal coordinates, specify

```
 $ZMAT DLC=.TRUE.  AUTO=.TRUE. $END
```

8.5 Performing a transition state search

Transition states are always more challenging to find than optimal geometries. Always `at least` a three-step procedure:

1. Guess a transition state structure and compute Hessian matrix (RUNTYP = HESSIAN). Check to be sure there is one imaginary mode approximating desired TS.

2. Perform the transition state search. Must supply computed Hessian matrix, copied from .dat file, as $HESS group. Also should specify $STATPT HESS=READ $END.

3. Check the result! Assuming the transition state search converges, run another frequency calculation to confirm that there is one and only one imaginary mode, and that it corresponds to desired TS.

9 Plane waves and core potentials

9.1 Hydrogen atom in a box

9.2 Periodic boundary conditions

9.3 Supercells - Cartesian and fractional coordinates

9.4 Gaussian vs. Vasp

9.5 Vasp POSCAR

9.6 Vasp INCAR

9.7 Core electron treatment

9.7.1 OPW

9.7.2 PP

9.7.3 PAW

9.8 Comparing energies between calculations

9.9 Wavefunctions and charge densities

9.10 Exploring potential energy surfaces

10 Periodic electronic structure

10.1 Isolated vs. periodic systems

10.2 Bloch's theorem and qualitative band structure

10.3 Band folding

10.4 Multi-dimensional periodicity

10.5 Density of statues

10.6 Bravais lattices

10.7 Quantitative supercell calculations

10.8 Brillouin zone integration

10.8.1 k-point sampling

10.8.2 Fermi smearing

11 Practical supercell calculations

12 Surfaces

12.1 Surface planes

12.2 Slab models

12.3 Surface energy

12.4 Surface potentials and Fermi energies

12.5 Surface adsorption

12.6 Coverage-dependent adsorption

12.7 Reaction barriers

13 Implicit solvation

14 Density functional theory

14.1 Electron density ρ as fundamental quantity

14.2 Thomas-Fermi-Dirac model

14.3 Hartree-Fock-Slater model

14.4 Hohenberg-Kohn theorems

14.5 Kohn-Sham construction

14.6 Exchange-correlation functionals

So Kohn et al. showed that the DFT approach is theoretically well-grounded and provided one way to practically apply it. Promise is that if we can find an approximation to the (unknown) true v_{xc} with the right balance of simplicity and accuracy, we will have one sweet theory. Has to incorporate both exchange, like Slater tried to do, and correlation.

How to proceed? Lots of approaches, and jargon here is at least as bad as in wavefunction-based methods. Perdew 2006 describes the "Jacob's ladder" of approximations:

14.6.1 LDA

One well-defined limit is the homogeneous electron gas, and this is the usual starting point for modern approximate DFT methods. Assume exchange and correlation potentials at any given point depend only on the value of ρ there (or spin-up and spin-down ρ, if spin-polarized). We know from Slater and Dirac's work what the exchange potential is for this system.

It is possible to determine numerically the correlation energy for a given density from quantum Monte Carlo calculations. Ceperley and Alder (PRL 1980, 45, 566) did this to very high accuracy, and others (Vosko, Wilk, and Nusair, "VWN", and Perdew and Wang, "PW") fit these numerical results to analytical models in ρ. This combination of local exchange and correlation defines the LDA model.

LDA offers modest improvement over HFS for molecules. "Homogeneous" approximation pretty severe for an atom or molecule. Nonetheless, works surprisingly well for structures and charge distributions, but has problems in calculating accurate bond energies, typically overbinding. Also tends to underestimate the HOMO-LUMO gap in molecules and analogous band gap in solids.

14.6.2 GGA

14.6.3 Meta-GGA

14.6.4 Hyper GGA and hybrid functionals

- "Screened" exchange

14.6.5   Beyond hyper GGA

14.7   Implementations

14.8   Performance

15   Electron correlation methods