



Chem 137

Review of quantum and intro to basis functions

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Resources

- Grant and Richards, Chapter 2
- Foresman and Frisch, *Exploring Chemistry with Electronic Structure Methods* (Gaussian Inc., 1996)
- Cramer, Chapter 4
- Jensen, Chapter 3
- Leach, Chapter 2
- Ostlund and Szabo, *Modern Quantum Chemistry* (McGraw-Hill, 1982)

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Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

- **H** is the quantum mechanical Hamiltonian for the system (an operator containing derivatives)
- **E** is the energy of the system
- Ψ is the wavefunction (contains everything we are allowed to know about the system)
- $|\Psi|^2$ is the probability distribution of the particles (as probability distribution, $|\Psi|^2$ needs to be continuous, single valued and integrate to 1)

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Solving the Schrödinger Equation

- analytic solutions can be obtained only for very simple systems
- particle in a box, harmonic oscillator, hydrogen atom can be solved exactly
- need to make approximations so that molecules can be treated
- approximations are a trade off between ease of computation and accuracy of the result

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Expectation Values

- for every measurable property, we can construct an operator
- repeated measurements will give an average value of the operator
- the average value or expectation value of an operator can be calculated by:

$$\frac{\int \Psi^* \hat{O} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \langle O \rangle$$

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Variational Theorem

- the expectation value of the Hamiltonian is the variational energy

$$\frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} = E_{\text{var}} \geq E_{\text{exact}}$$

- the variational energy is an upper bound to the lowest energy of the system
- any approximate wavefunction will yield an energy higher than the ground state energy
- parameters in an approximate wavefunction can be varied to minimize the E_{var}
- this yields a better estimate of the ground state energy and a better approximation to the wavefunction

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Hydrogen atom on computer

- Pretend we don't know exact solution (almost always true in reality)
- Expand true wavefunction in set of *basis* functions:

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu}$$

- The more you have, the more accurate your approximation to ϕ , the better (lower) your energy.
- Every time you add an extra one, you must get a better (or at least, not worsen) your energy.
- The coefficients give overlap with exact wavefunction.

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Standard basis sets

- Use gaussian wavefunctions for simplicity (easy to find integrals)

$$g_s(\vec{r}) = (2\alpha / \pi)^{3/4} \exp(-\alpha r^2)$$

- ☐ α is a parameter determining width
- The bigger α , the sharper is the peak; smaller α means broader peak.
- Always normalized, i.e., integrates to 1
- Usually α fixed inside a basis function.

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Normalization

- To check normalization:

$$\int d^3r |g_s(r)|^2 = 1$$

- Make sure you know how to do this integral for spherical functions.

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Expectation values

- Calculate kinetic energy and potential energy.

$$\int d^3r |g_s(r)|^2 = 1$$

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Hydrogen atom for one Gaussian

- Choose α to be $\frac{1}{2}$.
- Find kinetic and potential energies and sum them.
- What does variational principle tell you about the answer?
- Overlap is about 0.3. What does overlap tell you?

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LCAO

- Linear combination of atomic orbitals.
- Even for one H atom, can use several Gaussians
- Exponents are fixed, but can combine with different weights.
- Use variational principle to show that finding the lowest energy is same as finding eigenvectors
- Basis functions often not orthogonal, so must keep track of overlap.

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H atom with two Gaussians

- Write solution as

$$\phi = \sum_{\mu} c_{\mu} \chi_{\mu} = c_A g_A(r) + c_B g_B(r)$$

- A and B are Gaussians with fixed exponents
- In A, choose α to be $\frac{1}{4}$, in B, choose α to be 2
- One is very sharp, the other is quite broad.
- Which has higher kinetic energy? Potential energy?

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Overlap integral

- Overlap integral is measure of how alike two functions are

$$\int d^3r g_A^*(r) g_B(r) = S_{AB}$$

- Normalized functions have $S_{AA}=1$
- Similar functions have S_{AA} close to 1
- Orthogonal functions have $S_{AB}=0$

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Operators become matrices

- E.g., the potential energy operator $V(r)$ with 2 basis functions
- First find matrix elements, e.g.,

$$\int d^3r g_A^*(r) V(r) g_B(r) = V_{AB}$$

- Then V becomes 2x2 matrix:

$$\begin{pmatrix} V_{AA} & V_{AB} \\ V_{AB} & V_{BB} \end{pmatrix}$$

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Overlap matrix

$$\hat{S} = \begin{pmatrix} 1 & S_{AB} \\ S_{AB} & 1 \end{pmatrix}$$

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Finding approximate eigenstates

- Want to minimize Hamiltonian expectation value for normalized wavefunctions
- Equivalent to diagonalizing H-SE.
- Eigenvalues are approximations to energies, eigenfunctions give the coefficients in ϕ
- This finds the LCAO that gives lowest energy for those basis functions.
- The cost of diagonalizing increases with (# basis fns)³
- With enough basis functions, energy is **converged**, so that error with exact solution is tiny, and much less than all other errors.
- A basis set is some given set of functions for each element.

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