

CME 599 / MSE 620 Fall 2006

Overview of Quantum Chemistry Methods

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Quantum Mechanics

- * Fundamental equation: time-independent Schrödinger equation $\mathcal{H}\psi = E\psi$

where \mathcal{H} is the Hamiltonian operator, ψ is the wave function, and E is the energy

- * This is an eigen- (value/vector) equation
- * If ψ_n & E_n are the complete set of solutions to the eigen-eqn., any linear combination of ψ_n is also a solution

$$\psi = \sum_{n=1}^{\infty} a_n \psi_n$$

- * Recall that $|\psi|^2 dx dy dz = \text{probability density}$

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Properties of Wave Function

- * The expectation value of any property defined by an operator \hat{A} for a wave function is given by

$$\langle A \rangle = \frac{\int d\tau [\psi^* \hat{A} \psi]}{\int d\tau [\psi^* \psi]}$$

Where the integrals are taken over all possible values of the independent variables

- * ψ must be quadratically integrable to be able to normalize the probability density
- * ψ must be single-valued, continuous, and the gradient of ψ must be continuous
- * The set of wave functions solving Schrodinger equation should be orthogonal \rightarrow

$$\int d\tau [\psi_i^* \psi_j] = \delta_{ij}$$

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Free Particle

- * Hamiltonian is an operator of general form:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V} \quad \text{where } \hat{V} = \text{potential operator}$$

- * For a free particle, $\hat{V} = 0$ and Sch. Eqn. is:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi$$

- * In 1-D, this becomes: $\frac{d^2}{dx^2} \psi + k^2 \psi = 0$ where $k^2 = 2mE / \hbar^2$

- * The general solution is:

$$\psi = A \cos(kx) + B \sin(kx) \quad \text{where } A \text{ \& } B \text{ are constants}$$

(E is not quantized for a free particle)

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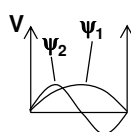
Particle in a 1D Box

- * Confine particle to 1D box of length L

✓ Inside box, $V = \text{constant} \rightarrow \psi = A \cos(kx) + B \sin(kx)$

✓ New boundary conditions introduced – potential energy is infinite outside of the box, so,

$\psi(x) = 0$ for $x \leq 0$ and $x \geq L$



• To have $\psi=0$ @ $x=0$, $A = 0 \rightarrow \psi = B \sin(kx)$

• $\psi(L) = 0 \rightarrow kL = n\pi$ where n is an integer \rightarrow energy is *quantized*

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 h^2}{8mL^2}$$

- * B is found by normalizing

$$\int_0^L \psi^* \psi dx = 1 = B^2 (L/2) \rightarrow \psi_n = \sqrt{2/L} \sin(n\pi x / L) \quad 5$$

Particle in a 3D Box

- * Generalizing to a 3D box with lengths L_x , L_y , and L_z in 3 directions leads to:

$$E_{n,m,l} = \frac{h^2}{8m} \left(\frac{n^2}{L_x^2} + \frac{m^2}{L_y^2} + \frac{l^2}{L_z^2} \right)$$

$$\psi_{n,m,l} = \sqrt{8/V} \sin(n\pi x / L_x) \sin(m\pi y / L_y) \sin(l\pi z / L_z)$$

- * For a cube of length L on each side, this reduces to:

$$E_{n,m,l} = \frac{h^2}{8mL^2} (n^2 + m^2 + l^2)$$

$$\psi_{n,m,l} = (2/L)^{3/2} \sin(n\pi x / L) \sin(m\pi y / L) \sin(l\pi z / L)$$

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One-electron Atom

- * Electrostatic attraction between electron (charge -1) and nucleus of charge Z leads to:

$$\left[-\frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi = E\psi$$

- * Separation of variables: $\psi = \psi_N \psi_e$

$$\underbrace{\left[-\frac{\hbar^2}{2(m_N + m_e)} \nabla_{cm}^2 \right]}_{\text{Nucleus equation}} \psi_N = E_N \psi_N \quad \left[-\frac{\hbar^2}{2\mu} \nabla_e^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi_e = E_e \psi_e$$

$\mu = \frac{m_N m_e}{m_N + m_e}$

- * Ignore nucleus equation (\rightarrow particle in box)

- * Solve electron eqn. in spherical coord \rightarrow orbitals

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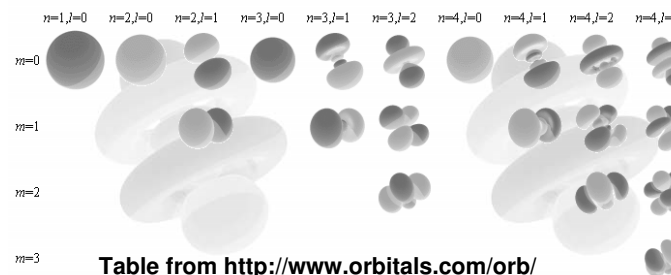
Atomic Orbitals

- * Energies depend on principal quantum no.

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \quad n = 1, 2, \dots$$

- * l and k determine orbital type (s, p, d, etc.)

- * $|\psi_e|^2 = \text{prob. density} - \text{isodensity surfaces below}$



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Spin and Electron Antisymmetry

- * Electrons possess spin -- a 2-state coordinate
- * Probability density of finding two particles at spatial + spin coordinates τ_1 and τ_2 is given by:

$$|\psi[\tau_1(1), \tau_2(2)]|^2 d\tau_1 d\tau_2$$

- * Because particles indistinguishable, though...

$$|\psi[\tau_1(1), \tau_2(2)]|^2 d\tau_1 d\tau_2 = |\psi[\tau_2(1), \tau_1(2)]|^2 d\tau_1 d\tau_2$$

- * This can be satisfied in two ways:

- ✓ Symmetric wavefunctions (bosons such as photons)

$$\psi[\tau_1(1), \tau_2(2)] = \psi[\tau_2(1), \tau_1(2)]$$

- ✓ Antisymmetric wavefunctions (fermions such as e⁻)

$$\psi[\tau_1(1), \tau_2(2)] = -\psi[\tau_2(1), \tau_1(2)]$$

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Helium Atom

- * Consider helium, with 2 electrons + 1 nucleus
- * Schrödinger equation (spin-free) is:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{1N}} - \frac{e^2}{4\pi\epsilon_0 r_{2N}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \psi = E\psi$$

- * In many-electron systems, orbital approximation
→ wave function constructed from single-electron spin orbitals, $S_\mu(i) = \phi_\mu(\mathbf{r}_i)\omega(\sigma_{\mu,i})$
- * Slater determinant is convenient way to combine – antisymmetric and uses all wave fcn

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} S_1(1) & S_2(1) \\ S_1(2) & S_2(2) \end{vmatrix}$$

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Helium Atom (2)

- * Spatial part of ground state orbital = “1s” and spin parts are α and β → $S_1 = 1s \alpha$ & $S_2 = 1s \beta$

- * Slater determinant →

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} 1s(1)1s(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

- * Energy found from wave function...

$$E = \frac{\int \psi \nabla^2 \psi d\tau}{\int \psi \psi d\tau}$$

$$= \frac{1}{2} \iint d\tau_1 d\tau_2 \{ [S_1(1)S_2(2) - S_1(2)S_2(1)] [\mathcal{D}_1 + \mathcal{D}_2 + \mathcal{J}] [S_1(1)S_2(2) - S_1(2)S_2(1)] \}$$

$$\text{where } \mathcal{D}_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0 r_{iN}} \text{ and } \mathcal{J} = \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

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Helium Atom (3)

- * Bearing in mind that each “core” Hamiltonian depends only on one set of coordinates,

$$E = 2\epsilon_{1s} + \frac{1}{2} \iint d\tau_1 d\tau_2 \{ [S_1(1)S_2(2) - S_1(2)S_2(1)] \mathcal{J} [S_1(1)S_2(2) - S_1(2)S_2(1)] \}$$

- * And because spin wavefncs are orthogonal,

$$E = 2\epsilon_{1s} + \iint d\tau_1 d\tau_2 \{ [1s(1)1s(2)] \mathcal{J} [1s(1)1s(2)] \}$$

↖ Electron-electron repulsion energy

- * For excited state with $S_1 = 1s \alpha$ and $S_2 = 2s \alpha$, an additional “exchange” integral appears

$$E = \epsilon_{1s} + \epsilon_{2s} + J_{1s,2s} - \underbrace{\iint d\tau_1 d\tau_2 \left\{ [1s(1)2s(2)] \frac{1}{r_{ij}} [2s(1)1s(2)] \right\}}_{K_{1s,2s}}$$

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Born-Oppenheimer Approximation

- * Interested in system of M nuclei and N electrons
- * “Should” solve Sch. Eq. for whole system, but $m_N \gg m_e \rightarrow$ can simplify equations
- * Separation of variables assumed: $\Psi = \Psi_N \Psi_e$
- * Nuclear positions are treated as *fixed* and the Schrödinger equation solved for electrons

$$\left[-\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i=1}^N \sum_{j=1}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right] \psi_e(\mathbf{r}; \mathbf{R}) = E(\mathbf{R}) \psi_e(\mathbf{r}; \mathbf{R})$$

- * Wave functions and energies depend on \mathbf{R}
- * “Forces” between nuclei due to $E(\mathbf{R})$

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Ab-initio Methods (1)

- * Methods based on direct determination of electron wave fcn. are *ab initio* methods
- * Solving Sch. Eqn. for all electrons is still difficult!
- * Problem: \mathcal{H} depends on all N electrons

$$\mathcal{H} = \underbrace{-\sum_{i=1}^N \left(\frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{A=1}^M \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} \right)}_{\mathcal{H}_{core}} + \sum_{i=1}^N \sum_{j=1}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

- * Hartree-Fock approach: use trial solution to approximate “field” of other electrons and iterate until “self-consistent” solution found (a.k.a. SCF)

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Ab-initio Methods (2)

- * HF method: solve Fock operator eigen-equation

$$\mathcal{F}\varphi_i = \epsilon_i \varphi_i \quad \text{where } \mathcal{F} = \mathcal{H}_{core} + \mathcal{J} - \mathcal{K}$$

where φ_i = molecular orbital (1 e⁻ in field of others), ϵ_i = orbital energy, \mathcal{J} = e⁻ repulsion operator, and \mathcal{K} is exchange operator for exchange of two electrons

- * Generalization of linear combination of atomic orbitals (LCAO) is used:

$$\varphi_i = \sum_{\mu=1}^N c_{i\mu} \chi_{\mu}$$

- * χ_i are basis functions similar to atomic orbitals \rightarrow MO state defined by vector \mathbf{c}_i

- * Entire set of MOs \rightarrow density matrix $P_{\mu\nu} = 2 \sum_{i=1}^{occ} c_{i\mu} c_{i\nu}$

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Ab-initio Methods (3)

- * HF method goal: find $\{\mathbf{c}\}$ to minimize $E \rightarrow$

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

$$\text{where } F_{\mu\nu} = \int \chi_{\mu} \mathcal{F} \chi_{\nu}; S_{\mu\nu} = \int \chi_{\mu} \chi_{\nu}; \text{ and } E_{ij} = \delta_{ij} \epsilon_i$$

- * The total energy is then given by:

$$E_{HF} = \sum_{\mu,\nu} P_{\mu\nu} H_{(core)\mu\nu} + \sum_{\mu,\nu,\lambda,\sigma} P_{\mu\nu} P_{\lambda\sigma} (J_{\mu\nu\lambda\sigma} - K_{\mu\nu\lambda\sigma}) + V_{nuclear}$$

- * Note: estimated $E \geq$ true E , so minimum is best!
- * Within HF method, there are many types of basis functions w/ time/accuracy tradeoff.
- * Slater-type orbitals – based on exact H orbitals
- * Gaussian-type orbitals – most common

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Ab initio Basis Sets

- * How to pick basis functions:

- ✓ Read! See what others have shown to work for systems like yours
- ✓ Try several – see how much E changes with increasing complexity

Table 1. Acronyms of the most commonly used basis sets

Basis set	Characteristics
STO-3G	A minimal basis set using three GTO to approximate each STO.
3-21G	A split valence basis set. Inner shell basis functions made of three GTOs. Valence orbitals are split into 2 and 1 GTOs.
6-31G	A split valence basis set. Inner shell basis functions made of six GTOs. Valence orbitals are split into 3 and 1 GTOs.
6-31G(d) or 6-31G*	The 6-31G basis set with the addition of six <i>d</i> -type polarization functions to non-hydrogen atoms.
6-31G(d,p) or 6-31G**	The 6-31G(d) basis set with the addition of <i>p</i> -type polarization functions to non-hydrogen atoms.
6-31G + (d,p) or 6-31 + G**	The 6-31G(d,p) basis set with the addition of <i>s</i> - and <i>p</i> -type diffuse functions to the atoms of first and second rows.
6-31G + + (d,p) or 6-31 + + G**	The 6-31G(d,p) basis set with the addition of a set of <i>s</i> - and <i>p</i> -type diffuse functions to the atoms of first and second rows and a set of <i>s</i> -type functions to hydrogen.
6-311G	A split valence basis set. Inner shell basis functions made of six GTOs. Valence orbitals are triply split into 3, 1, and 1 GTOs.
D95	Dunning/Huzinaga full double zeta.
CEP-121G	Stevens/Basch/Krauss ECP triple-split basis.
LanL2DZ	D95V on first row and Los Alamos ECP plus DZ on Na-Bi.
SDD	D95V up to Ar and Stuttgart/Dresden ECPs on the remainder of the periodic table.
cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z	Dunning's correlation consistent basis sets (double, triple, quadruple, quintuple-zeta and sextuple-zeta, respectively).

Table from C. A. Tsipis, *Comments Inorg. Chem.* **2004**, 25: 19.

Improving Upon HF Method

- * Problem with HF: correlations between electrons neglected with SCF method

$$E_{\text{correlation}} = E_{\text{exact}} - E_{\text{HF}} < 0$$

- * Methods to refine E (beware of cost!):

- ✓ Variational: Include excited MOs in addition to “ground state” MOs of HF method; use linear combination and minimize E by changing {*c_i*}. Quality detd. by # of excited electrons included
- ✓ Perturbational: Perturb Hamiltonian by replacing HF operator with $\mathcal{F}_0 + \lambda[\mathcal{V}(\lambda) - \mathcal{F}_0]$; $E = E_0 + \lambda E_1 + \lambda^2 E_2$ etc. Møller-Plesset methods most common: MP2 2nd order, MP3 3rd order.

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Density Functional Theory

- * Alternative approach: treat energy as *functional* of electron density $\rho(\mathbf{r}) \rightarrow$ density func. Theory
- * DFT energy similar to HF, but exchange and correlation treated as *empirical* functionals

$$E_{\text{DFT}} = \sum_{\mu,\nu} P_{\mu\nu} H_{\mu\nu} + \sum_{\mu,\nu,\lambda,\sigma} P_{\mu\nu} P_{\lambda\sigma} J_{\mu\nu\lambda\sigma} + \underbrace{E_X(\rho)}_{\text{exchange}} + \underbrace{E_C(\rho)}_{\text{correlation}} + V_{\text{nuc}}$$

- * DFT uses different (Kohn-Sham, KS) way of developing orbitals; expense comparable to HF
- * Improved functionals use gradients – generalized gradient approx. (GGA) uses $\nabla\rho(\mathbf{r})$ and meta-GGA uses $\nabla^2\rho(\mathbf{r})$

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Faster! – Semi-empirical MO

- * Majority of time in HF method is spent evaluating integrals in Fock matrix
- * Semi-empirical MO lump “core” electrons into nucleus and performed detailed calculation with Slater orbitals on valence electrons only
- * Also, overlap integrals simplified: $\mathbf{S} = \mathbf{I} \rightarrow$ HF equation simplified to: $\mathbf{FC} = \mathbf{CE}$
- * Various models available, differing in:
 - ✓ Level of overlap included in the Hamiltonian
 - ✓ Empirical terms found by parameterization w/ data
- * Semi-empirical MO faster but less accurate

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Table 2.2. MNDO, PM3, AM1, MNDOC, MNDO/d, SAM1, and SAM1D Elemental Parameter Sets

Element	AM1	PM3	MNDO	MNDO/d	MNDOC	SAM1	SAM1D	Element
H	•	•	•	◊	•	•	◊	H
Li		•	•	◊	•			Li
Be		•	•	◊				Be
B	•	•	•	◊				B
C	•	•	•	◊				C
N	•	•	•	◊	•	•	◊	N
O	•	•	•	◊	•	•	◊	O
F	•	•	•	◊	•	•	◊	F
Na				•				Na
Mg		•						Mg
Al	•	•	•	•				Al
Si	•	•	•	•		•	◊	Si
P	•	•	•	•		•	◊	P
S	•	•	•	•		•	◊	S
Cl	•	•	•	•		•	•	Cl
Ca								Ca
Fe						•	◊	Fe
Cu						•	◊	Cu
Zn	•	•	•	•				Zn
Ga		•						Ga
Ge	•	•	•					Ge
As	•	•	•					As
Se	•	•	•					Se
Br	•	•	•	•		•	•	Br
Cd		•		•				Cd
In		•						In
Sn	•	•	•					Sn
Sb	•	•	•					Sb
Te	•	•	•					Te
I	•	•	•	•		•	◊	I
Hg	•	•	•	•				Hg
Tl		•						Tl
Pb		•	•					Pb
Bi		•						Bi

<http://helix.nih.gov/apps/structbio/ampac/ampacmanual/methods.html>

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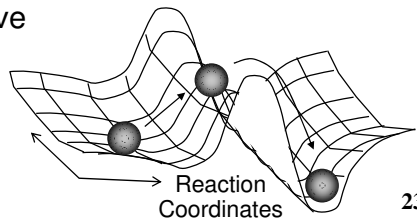
Quantum Chemistry Applications

- * Quantum chemical methods best for isolated molecules or a few molecules with bonding
- * Many properties can be calculated
- * Geometry optimization
 - ✓ Nuclear coordinates (\mathbf{R}^M) are variables changed to minimize total energy
 - ✓ Method (ab initio vs. semi-empirical) determines E
 - ✓ Many algorithms available (NR, simplex, etc)
 - ✓ Optimizing in 3M-dimensional space
 - ✓ Usually only local minima found → search for global minimum and watch for saddle points

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QC Applications (2)

- * Single-Point Energy Calculation
 - ✓ E or energy of formation with nuclei fixed
 - ✓ Ab initio or DFT methods best
- * Predicting barrier / reaction path
 - ✓ E vs. \mathbf{R}^M → potential energy surface
 - ✓ Saddle point between two states → barrier
 - ✓ Locate saddle point by moving from stable state to higher energy / negative eigenvalue of \mathbf{H}
 - ✓ $H_{ij} = d^2V/dR_i dR_j$



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QC Applications (3)

- * Observing electron density
 - ✓ Isodensity plots of $\phi^*\phi$ (elec. probability density)
 - ✓ Highest occupied (HOMO) and lowest unoccupied (LUMO) help to understand reactivity
- * Atomic charges
 - ✓ Mulliken → overlaps between orbitals used to assign partial charge from orbital to nuclei

$$Q_\mu = P_{\mu\mu}S_{\mu\mu} + \sum_{\mu \neq \nu} \frac{1}{2}(P_{\mu\nu}S_{\mu\nu} + P_{\nu\mu}S_{\nu\mu})$$

$$Q_A^{\text{Mulliken}} = Z_A - \sum_{\mu \in A} Q_\mu$$

- ✓ Better methods available for large basis sets

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QC Applications (4)

- * Dipole moments from nuc. coord. + e⁻ density

$$\mu = e \sum_{A=1}^M Z_A \mathbf{R}_A - r \int P_i(\mathbf{r}) \mathbf{r} d\tau$$

- * Electrostatic potential $V_E = \sum_{A=1}^M \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{d\mathbf{r}' \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$

- * Vibrational frequencies

✓ From numerical Hessian matrix, $H_{ij} = d^2V/dR_i dR_j$

✓ Mass-weighted $\mathbf{H} \rightarrow H_{ij}^m = H_{ij}/(m_i m_j)^{1/2}$

✓ Eigenvalues of H are ϵ_i values $\rightarrow \nu_i = \epsilon_i^{1/2}/(2\pi c)$

- * NMR \rightarrow gauge-induced atomic orbitals (GIAO) method best approach \rightarrow shielding $\rightarrow \delta$

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Molecular Mechanics

- * To accelerate even more than MO method, measure $E(\mathbf{R}^{nuc})$ and approximate with function
- * Functions must be parameterized with ab initio calculations or with experimental data
- * E depends on interatomic separation, bond stretch, bond bend, torsion, etc.
- * Potentials (or “forcefields”) can be transferred between “similar” molecules
- * Geometry optimization is fast and classical functions \rightarrow molecular dynamics / Monte Carlo

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MM Makes Limited Predictions

- * In addition to accuracy of energy / configuration, MM limited in predicting properties
- * Electron density not explicitly represented

Table 1.1. Information Available from Computational Methods

Data Item	Molecular Mechanics	Semiempirical	ab initio
Heat of Formation	•	•	•
Entropy of Formation	•	•	•
Free Energy of Formation	•	•	•
Heat of Activation	•	•	•
Entropy of Activation	•	•	•
Free Energy of Activation	•	•	•
Heat of Reaction	•	•	•
Entropy of Reaction	•	•	•
Free Energy of Reaction	•	•	•
Strain Energy	•	†	†
Vibrational Spectra	•	•	•
Dipole Moments	•	•	•
Optimized Geometries	•	•	•
Electronic Bond Order	•	•	•
Electronic Distribution	•	•	•
Mulliken Pop. Analysis	•	•	•
Transition State Location	•	•	•

• Property Predicted
† Indirectly Available

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Table from AMPAC Manual: <http://www.semichem.com/ampacmanual/intro.html>

Implementations of QC Methods

Program	Ab initio?	DFT ?	MO ?	MM ?	Platforms	GUI?	Commercial?
Materials Studio	X	X	X	X	WU	X	\$\$\$
HyperChem	X	X	X	X	W	X	\$
Spartan	X	X	X	X	WMU	X	\$\$
NWChem	X	X		X	U		
ArgusLab			X	X	W	X	
Gaussian 03	X			X	WMU	X	\$\$
GAMESS	X	X			U		
Chem3D			X	X	W	X	\$
MOPAC			X		WU		
MPQC	X				U		
Ampac			X		WMU	X	

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Quantum Chemistry Summary

- * First principles atomic/molecular properties predicted by QM → Schrödinger equation
- * QM needed to accurately predict properties dependent on electrons – charge, reactions, etc.
- * Hartree-Fock and DFT based methods directly attempt to approximate wave functions
- * Semi-empirical MO methods increase speed at expense of accuracy and predictive ability
- * Molecular mechanics captures dependence of energy on configuration and is very fast, but dispenses with electron densities