Chemistry 334
Part 2: Computational Quantum Chemistry

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1. Definition

Computational chemistry is an area of theoretical chemistry whose focus is the use and development of efficient mathematical approximations and computer programs to obtain results relative to chemical problems. Examples of properties that can be calculated include total energies, molecular geometries, dipole and quadrupole moments, vibrational frequencies, reaction cross-sections, thermochemical data and diverse spectroscopic quantities. Computational *quantum* chemistry uses mathematical equations and approximations derived from quantum mechanics.

2. Introduction

Exact analytical solutions to the Schrödinger equation only exist for the simplest of quantum mechanical systems like the particle in a box, rigid rotor, harmonic oscillator, and the hydrogen atom. Calculations on more complex systems, like many-electron atoms and molecules, require approximations to be made. There exist numerous methods available to computational quantum chemists that employ differing levels of approximation and thus differ in accuracy and cost (time and computer resources required). The method one chooses for a specific problem is largely determined by the accuracy desired, computer resources available, and length of time. Generally, the cost of a calculation increases dramatically with increasing system size and level of accuracy (discussed more specifically below). Numerical solutions of extremely high accuracy are still possible, but may require considerable computational resources. The methods discussed here are called *ab initio* ("from the beginning") because they do not include empirical parameters or experimental data and are derived directly from the postulates of quantum mechanics.

There are 3 main concepts that should be kept in mind when obtaining approximate solutions to the quantum mechanical Schrödinger equation: (a) the Born-Oppenheimer approximation, which leads to the idea of a potential energy surface, (b) the expansion of the many-electron wavefunction in terms of Slater determinants, i.e., the "method", and (c) the representation of Slater determinants by molecular orbitals, which are constructed from atom-centered Gaussian-type functions, i.e., the "basis set".

3. Potential Energy Surfaces

The primary goal of computational quantum chemistry is to solve the Schrödinger equation (SE), $\hat{H}\Psi = E\Psi$, where E is the total energy of the molecular system, Ψ is the wavefunction describing the position and momentum of all the particles, and the Hamiltonian operator $\hat{H}$ specifies the kinetic and potential energies of all the particles in the system of study due to the Coulomb interactions present, both nuclei and electrons (in atomic units):

$$\hat{H} = -\frac{1}{2}\sum_{i}^{electrons}\nabla_i^2 - \frac{1}{2}\sum_{\alpha}^{nuclei}\frac{1}{M_\alpha}\nabla_\alpha^2 - \sum_{i}^{electrons}\sum_{\alpha}^{nuclei}\frac{Z_\alpha}{r_{i\alpha}} + \sum_{i>j}^{electrons}\frac{1}{r_{ij}} + \sum_{\alpha>\beta}^{nuclei}\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \qquad (1)$$

The terms in the above equation correspond to: kinetic energy of the electrons, kinetic energy of the nuclei, electron-nuclear attraction, electron-electron repulsion, and nuclear-nuclear repulsion. Solving the full many-electron, many-nuclei Schrödinger equation is a formidable task and in general does not have analytical solutions. Fortunately the two types of particles in molecular systems, nuclei and electrons, have very different masses and hence have vastly different timescales under which their motion takes place. For example, in the case of the hydrogen molecule, the mass of the proton is 1836 times larger than that of the electron. In this case heavy implies slow and thus to a high degree of accuracy the nuclear motion can be separated from the electron motion, i.e., from the electrons' point of view they move about in the presence of fixed (stationary) nuclei and from the nuclei's point of view as they move (vibrate/rotate), the electrons adjust smoothly and instantaneously to their motion. This is the Born-Oppenheimer approximation, which has the practical effect of splitting the full SE into two equations: one for nuclear motion and one for electronic motion. It is the latter one, $\hat{H}^{el}\Psi^{el} = E_{el}\Psi^{el}$ which is the focus of most quantum chemists. The electronic Hamiltonian operator $\hat{H}^{el}$ has a similar form as the full $\hat{H}$ given in Eq. (1) but with the second term (nuclear kinetic energy) omitted and the last term (nuclear-nuclear Coulomb repulsion) is now just a constant for a particular choice of molecular geometry.

The electronic Schrödinger equation is then solved as a function of the (fixed) relative nuclear positions (the *internal* coordinates), all $3n$-6 of them ($3n$-5 for diatomics; n is the number of atoms), and the resulting values of E_{el} (one for each unique inter-nuclear orientation, i.e., molecular structure or geometry) defines the potential energy surface (PES), $V(\mathbf{R})$. This represents the potential energy for all nuclear motion, i.e., all the forces that the nuclei experience as a function of geometry. Solutions of the nuclear motion SE yield a molecule's rotational and vibrational spectrum (these depend on the gradients, Hessians, and higher derivatives of the PES), and the topology of this surface (minima, barriers, valleys, etc.) can lead to the determination of reaction rates and mechanisms.

A potential energy surface can range in complexity from a relatively simple one-dimensional diatomic potential energy curve (V vs. R) to a multidimensional hypersurface of dimensionality $3n$-6. In fact a triatomic molecule already possesses too many internal coordinates (3) to simultaneously display the variation of its energy with its two bond lengths and angle, e.g., V vs. R_1, R_2, and θ. One is immediately faced with visualizing only special "cuts" or "slices" of the full potential energy surface. Locations

of energy minima yield the equilibrium positions of reactants, products, and intermediates. Energy maxima can be associated with transition states. A reaction path can be defined as the lowest energy route between reactants and products via a transition state. It can be visualized as a streambed leading uphill out of the lake or valley representing the reactants over a saddle in the mountains down to another valley or lake representing the products.

The minima on a PES are defined by zero first derivatives (gradients) of the potential energy with respect to all internal coordinates, i.e., $\frac{dV}{dR_i} = 0$; $i = 1, 2, \ldots, 3n - 6$. In addition, all the second derivatives are positive (uphill in all directions). A transition state also has all zero gradients, but one of the second derivatives is negative, which corresponds to the downhill direction of the reaction coordinate towards reactants and products. The calculation of equilibrium structures is in principle straightforward since one only needs to search "downhill". Of course there is no guarantee that a minimum that is found corresponds to the structure with the globally lowest energy (it could be a stable intermediate). Calculating the structure of transition states can be much more difficult since they must have one and only one negative second derivative. If a true transition state is located, there is also no guarantee that it connects the reactants and products of interest.

Several techniques are available for characterizing the reaction path that connects reactants with products on the PES. In the *distinguished reaction coordinate* approach, the reaction coordinate is assumed to be well described by changes in a single internal coordinate of the molecular system, e.g., a bond length or angle. This special coordinate is then incrementally changed while minimizing the energy with respect to all of the other coordinates. This method thus requires calculation of first derivatives of the PES. The resulting one-dimensional curve is an approximation to the actual minimum energy reaction path that passes through the transition state on to products. The maximum in this curve corresponds to an approximate transition state structure. The success of this method obviously hinges on the specific choice for the reaction coordinate. A second, more rigorous method used for defining the reaction path is the *intrinsic reaction coordinate* (IRC) method, and it most closely describes the dynamics of the nuclear motion in the reaction. The IRC is defined by the line of steepest descent followed down (forwards towards products and backwards towards reactants) from the transition state using mass-weighted coordinates. This method generally requires calculation of both the first and second derivatives of the PES along the path.

4. Approximating the wave function (*The Method*)

Outside of the Born-Oppenheimer approximation, one of the two most important approximations in solving the electronic Schrödinger equation involves the expansion of the many-electron wave function:

$$\Psi^{el} = \sum_i d_i \Phi_i = d_0 \Phi_0 + d_1 \Phi_1 + d_2 \Phi_2 + \cdots \tag{2}$$

Where the d_i's are just numbers (expansion coefficients) and the Φ_i's are Slater determinants, e.g.,

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$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1\alpha(1) & \phi_1\beta(1) & \phi_2\alpha(1)\dots & \phi_M\beta(1) \\ \phi_1\alpha(2) & \phi_1\beta(2) & \phi_2\alpha(2)\dots & \phi_M\beta(2) \\ \dots & \dots & \dots & \dots \\ \phi_1\alpha(N) & \phi_1\beta(N) & \phi_2\alpha(N)\dots & \phi_M\beta(N) \end{vmatrix} \tag{3}$$

where N is the total number of electrons, M is the size of the basis set (see below), α/β are spin functions, and the ϕ_i are spatial functions, i.e., molecular orbitals (note: a spatial function multiplied by a spin function yields what is called a spin orbital). Interchanging any two rows or columns of a determinant changes its sign, and thus a Slater determinant yields the correct anti-symmetry of the electronic wave function. In particular this insures that the wave function obeys the Pauli Exclusion Principle (no two electrons can occupy the same spin orbital).

So the main question is how many determinants do we include in the sum of Eq. (2)? If we restrict ourselves to just a single determinant, i.e., Φ_0, we obtain what's called the Hartree-Fock (HF) approximation. This is a variation method (the resulting energy is an upper bound to the exact energy) where the optimal set of molecular orbitals (those yielding the lowest energy) are determined in a process called the self-consistent field (SCF) procedure. In regards to the Hamiltonian operator of Eq. (1), the HF approximation is directly related to how the electron-electron repulsion interaction is treated. This term refers to the instantaneous repulsion between individual pairs of electrons. In the HF approximation, however, each electron experiences only the average repulsion of all the remaining electrons. The energy effect of these "missing" repulsions between pairs of electrons is called the *correlation energy*. It is formally defined as the difference between the HF energy and the exact solution of the Schrödinger equation.

Moving beyond the HF approximation involves recovering the effects of electron correlation, which implies adding additional Slater determinants to the expansion of Eq. (2). There are many methods to do this and the number of acronyms grows at an alarming rate. There are three main categories among those methods that involve a wavefunction (methods called density functional theory (DFT) are currently also popular among chemists, but will not be discussed in this document): perturbation theory, configuration interaction, and coupled cluster theory. The choice of method is dictated by computational speed/cost (i.e., measured as actual time to completion), accuracy, and the application under study.

In Møller-Plesset (MP) perturbation theory, electron correlation is assumed to be a small effect and its impact on the energy is calculated to various orders of approximation, e.g., 2nd order MP perturbation theory or MP2, 3rd order (MP3), 4th order (MP4), etc. (MP1 is equivalent to HF theory). At infinite order the energy is typically equal to the exact solution of the Schrödinger equation (however there is no guarantee that this series is actually convergent). The computational cost increases strongly with each successive order of perturbation theory.

Configuration interaction (CI) methods are generally a straightforward application of the linear variation method. *This method essentially states that no matter what wave function is used for the ground state, the energy is always greater than or equal to the*

true energy. A linear combination of Slater determinants is constructed and the coefficients multiplying each determinant are varied to yield the lowest energy. Variants of CI theory are capable of very high accuracy, but generally the length of the expansion has to be very long (hundreds of thousands, millions, or more), which can lead to large computational expense. Common applications of CI theory are CISD (singles and doubles CI) and MRCI (multi-reference CI).

In coupled cluster (CC) theory an exponential operator is used in constructing the expansion of determinants in Eq. (2). This leads to accurate, compact wave function expansions yielding accurate electronic energies. Common variants are the CCSD (singles and doubles CC) and CCSD(T) (CCSD with approximate treatment of triple excitations) methods.

5.   Representing the molecular orbitals (*The Basis Set*)

In order to build a wave function in terms of Slater determinants, the molecular orbitals first have to be defined. The most common approach is to approximate each molecular orbital by an expansion of functions called the *basis set*:

$$\phi_i = \sum_k^M C_{ki} \chi_k \qquad (4)$$

The molecular orbital coefficients C_{ki} are determined variationally in the SCF procedure. The basis functions χ_k are centered on each atom of the molecule and mimic solutions of the hydrogen atom, i.e., *s* orbitals, *p* orbitals, etc. Hence this is called the linear combination of atomic orbitals-molecular orbital (LCAO-MO) approximation. The individual basis functions are typically constructed of Gaussian-type functions ($e^{-\alpha r^2}$) of various widths (determined by the values of α) multiplied by spherical harmonic functions (to obtain *p* functions, *d* functions, etc.). The basis functions χ_k can be either single Gaussian-type functions or they can themselves be expansions of Gaussians with fixed expansion coefficients (called *contracted* Gaussians). Individual Gaussian functions are often referred to as *primitive* Gaussians. In either case both the expansion coefficients (called contraction coefficients) and the exponents are previously optimized for a given atom in either a HF calculation or some type of correlated calculation. The basis sets are tabulated and made available for users of computational chemistry programs (that's you!).

There are a very large number of basis sets that one can choose from for *ab initio* (from first principles, i.e., no empirical parameters) molecular quantum chemistry calculations. One family of sets are referred to as *Pople-style basis sets*, coined for Prof. John Pople who won the Nobel Prize in Chemistry in 1998 for making quantum chemistry readily accessible to chemists through his series of Gaussian computer programs. Pople-style basis sets generally have a notation like *6-31G*, which translates to: a single contracted Gaussian-type function consisting of 6 individual functions (*primitives*) is included to describe the electrons in low energy orbitals (e.g., the 1s electrons of carbon), and 2 contracted Gaussians to describe the valence electrons; one consists of 3 primitives contracted together and the other is a single, 1 *uncontracted* Gaussian-type function. The definition of Pople sets like 3-21G and 6-311G follow

analogously. Basis sets for accurate calculations require the addition of *polarization functions*, i.e., functions of at least one angular momentum higher than what is occupied in the bonding atoms that can be utilized to polarize the bond. In H_2 a *p*-type function can polarize the σ bond, whereas in N_2 a *d*-type function is the primary polarization function. The Pople-style notation is often modified by asterisks to denote polarization functions, i.e., 6-31G* denotes the additional of a *d*-type function to the basis (all 6 Cartesian components) while 6-31G** denotes a *p*-type function on the H atoms and a *d*-type function on all other atoms. Sometimes a more explicit notation is used, i.e., 6-31G(d) and 6-31G(d,p) is equivalent to 6-31G* and 6-31G**.

The second common choice of basis sets is the family of *correlation consistent* basis sets. These basis sets have the unique property of forming a systematically convergent set, i.e., they range from small to large and a series of calculations with a sequence of these basis sets can lead to accurate estimates of the complete basis set (CBS) limit. This corresponds to the exact solution of the Schrödinger equation within the model chosen above, e.g., the exact HF, MP2, or CCSD(T) energy. The notation for these basis sets has the form cc-pV*n*Z, which stands for 'correlation consistent polarized valence *n*-zeta' and *n* = D, T, Q, 5 … (double/triple/quadruple/quintuple/ etc). The cc-pVDZ (Double-Zeta) basis set is similar in quality to the Pople-style 6-31G(d, p) set, while the cc-pVTZ (Triple-Zeta) set would be somewhat related to 6-311G(2df, 2pd).

6. Computational Cost

The obvious question after all this discussion is why not use the very best wave function method with the largest cc-pV*n*Z basis set available and hence get very close to the exact solution of the electronic Schrödinger equation? Unfortunately it comes down to how powerful of a computer you have and how long you are willing to wait for your answer. From the form of the Slater determinant in Eq. (3), one can infer that the size of a calculation will scale with the number of electrons and the size of the basis set. Each wave function method effectively includes various numbers of determinants and in principle the relative "cost" of a calculation with a given method can be simply related to the size of the basis set employed, e.g.,

Method	Scaling of Cost
HF	$M^2 - M^3$
MP2	M^5
CCSD	M^6
CCSD(T)	M^7

In the above table *M* is the number of basis functions. Hence for the same molecule and basis set, a MP2 calculation is approximately 100 times more computationally demanding than a HF calculation. A CCSD(T) calculation would then be about 100 times more expensive than MP2. On the other hand, within a given method, e.g., MP2, increasing the size and accuracy of the basis set can substantially increase the time to solution and the computational requirements, e.g., doubling the basis set size will increase the

computational cost by roughly 2^5 or 32. The choice of method and basis set is a balance between speed and accuracy. Often the old adage, "you get what you pay for", is true, but fortunately for many systems of chemical interest inexpensive methods like HF and MP2 yield excellent results (as judged by how close they reproduce known experimental values).

7. Reading Assignments

(1) Chapter 21 of Engel and Reid, <u>Physical Chemistry</u>, p 453
(2) Chapter 27 by Dr. Warren Hehre in Engel and Reid, <u>Physical Chemistry</u>, p 597.