

A Short Summary of Quantum Chemistry

Quantum Chemistry is (typically) based on the non-relativistic Schroedinger equation, making the Born-Oppenheimer approximation. The Schroedinger equation is

$$H_{\text{total}} \Psi_{\text{total}} = E \Psi_{\text{total}}$$

Where

E = an allowed energy of the system (the system is usually a molecule).

Ψ_{total} = a function of the positions of all the electrons and nuclei and their spins.

H_{total} = a differential operator constructed from the classical Hamiltonian $H(p,q) = E$ by replacing all the momenta p_i with $(\hbar/2\pi i) \partial/\partial q_i$ as long as all the p and q are Cartesian. If you would prefer to use a non-Cartesian coordinate system it is tricky to construct the correct quantum mechanical H . The standard way to make Hamiltonians for arbitrary coordinate systems is to use the "Podolsky trick". For a system of nuclei and electrons in a vacuum with no external fields, neglecting magnetic interactions, using atomic units:

$$H_{\text{total}} = -\frac{1}{2} \sum \nabla_i^2 / M_i - \frac{1}{2} \sum \nabla_n^2 + \sum Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j| - \sum Z_i / |\mathbf{R}_i - \mathbf{r}_n| + \sum 1 / |\mathbf{r}_m - \mathbf{r}_n|$$

The Born-Oppenheimer approximation is to neglect some of the terms coupling the electrons and nuclei, so one can write:

$$\Psi_{\text{total}}(\mathbf{R}, \mathbf{r}) = \Psi_{\text{nuclei}}(\mathbf{R}) \Psi_{\text{electrons}}(\mathbf{r}; \mathbf{R})$$

$$H_{\text{total}} \cong T_{\text{nuclei}}(\mathbf{P}, \mathbf{R}) + H_{\text{electrons}}(\mathbf{p}, \mathbf{r}; \mathbf{R})$$

(ignores the dependence of $H_{\text{electrons}}$ on the momenta of the nuclei \mathbf{P})

then solve the Schroedinger equation for the electrons (with the nuclei fixed). The energy we compute will depend on the positions \mathbf{R} of those fixed nuclei, call it $V(\mathbf{R})$:

$$H_{\text{electrons}}(\mathbf{p}, \mathbf{r}; \mathbf{R}) \Psi_{\text{electrons}}(\mathbf{r}; \mathbf{R}) = V(\mathbf{R}) \Psi_{\text{electrons}}(\mathbf{r}; \mathbf{R})$$

Now we go back to the total Hamiltonian, and integrate over all the electron positions \mathbf{r} , ignoring any inconvenient terms, to obtain an approximate Schroedinger equation for the nuclei:

$$\langle \Psi_{\text{electrons}}(\mathbf{r}; \mathbf{R}) | H_{\text{total}} | \Psi_{\text{electrons}}(\mathbf{r}; \mathbf{R}) \rangle \cong H_{\text{nuclei}} = T_{\text{nuclei}}(\mathbf{P}, \mathbf{R}) + V(\mathbf{R})$$

Both approximate Schroedinger equations are still much too hard to solve exactly (they are partial differential equations in $3N_{\text{particles}}$ coordinates), so we have to make more approximations. V_{nuclei} is usually expanded to second order \mathbf{R} about a stationary point \mathbf{R}_0 :

$$V_{\text{nuclei}} \cong V_{\text{nuclei}}(\mathbf{R}_0) + \frac{1}{2} \sum (\partial^2 V / \partial R_i \partial R_j) (R_i - R_{0i})(R_j - R_{0j})$$

and then the translations, rotations, and vibrations are each treated separately, neglecting any inconvenient terms that couple the different coordinates. In this famous “rigid-rotor-harmonic-oscillator (RRHO)” approximation, analytical formulas are known for the energy eigenvalues, and for the corresponding partition functions Q , look in any P.Chem. text.

This approximate approach has the important advantage that we do not need to solve the Schrodinger equation for the electrons at very many R 's: we just need to find a stationary point R_0 , and compute the energy and the second derivatives at that R_0 . Many computer programs have been written that allow one to compute the first and second derivatives of V almost as quickly as you can compute V . For example, for the biggest calculation called for in problem 3 with 10 atoms and $3 \times 10 = 30$ coordinates R_i , it takes about half a minute on an Athena machine to compute $V_{\text{nuclei}}(R_0)$ and only about 13 more minutes to compute the $30 \times 30 = 900$ second derivatives ($\partial^2 V / \partial R_i \partial R_j$). If you tried to do this naively by finite differences, it would take about 15 hours to arrive at the same result (and it would probably be less accurate because of finite differencing numerical errors.) The analytical first derivatives are used to speed the search for the stationary point (e.g. the equilibrium geometry) R_0 . Often the geometry and the second derivatives are calculated using certain approximations, but the final energy $V(R_0)$ is computed more accurately (since thermo and rates are most sensitive to errors in $V(R_0)$, and even poor approximations often get geometry and frequencies close to correct).

So... as long as a second-order Taylor expansion approximation for V is adequate we are in pretty good shape. Molecules and transition states with “large amplitude motions” (i.e. the Taylor expansion is not adequate) are much more problematic, dealing with them is an active research area. Fortunately, there are many systems where the conventional second-order V , RRHO approximation is accurate.

But how do we compute $V(R)$ at any geometry R ? We want to solve

$$H_{\text{electrons}}(\mathbf{p}, \mathbf{r}; \mathbf{R}) \Psi_{\text{electrons}}(\mathbf{r}; \mathbf{R}) = V(\mathbf{R}) \Psi_{\text{electrons}}(\mathbf{r}; \mathbf{R})$$

where in a vacuum, in the absence of fields, and neglecting magnetic effects

$$H_{\text{electrons}}(\mathbf{R}) = -\frac{1}{2} \sum \nabla_n^2 + \sum Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j| - \sum Z_i / |\mathbf{R}_i - \mathbf{r}_n| + \sum 1 / |\mathbf{r}_m - \mathbf{r}_n|$$

and because the electrons are indistinguishable Fermions any permutation of two electrons must change the sign of $\Psi_{\text{electrons}}$ (this is a really important constraint called the Pauli exclusion principle, it is the reason for the periodic table) and because spin is a good quantum number we have more constraints:

$$S^2 |\Psi_{\text{electrons}}\rangle = S(S+1) |\Psi_{\text{electrons}}\rangle$$

$$S_z |\Psi_{\text{electrons}}\rangle = M |\Psi_{\text{electrons}}\rangle$$

We can write $\Psi_{\text{electrons}}$ in a form that will guarantee it satisfies Pauli:

$\Psi_{\text{electrons}}(x_1, x_2, x_3, \dots, x_N) = \sum C_{m_1 m_2 m_3 \dots m_N} |\phi_{m_1}(x_1) \phi_{m_2}(x_2) \phi_{m_3}(x_3) \dots \phi_{m_N}(x_N)|$
 where the symbol $|\dots|$ means to construct the correctly antisymmetrized “Slater determinant”. The “molecular orbitals” $\phi_m(x_i)$ are scalar functions of the position and spin coordinates of one electron. They are usually written as a sum of “atomic orbitals” χ :

$$\phi_m(x, y, z, s) = |s_z\rangle \sum D_{mn} \chi_n(x, y, z)$$

The atomic orbitals are almost always taken to have the form of sums of Gaussians centered on one of the atoms times a polynomial in the electron coordinates relative to that atom:

$$\chi_n(\mathbf{r}) = \sum N_{nl} \exp(-\alpha_{nl}(|\mathbf{r}-\mathbf{R}_{i(n)}|^2)) P_l(\mathbf{r}-\mathbf{R}_{i(n)})$$

There are conventional sets of these atomic orbitals that are used, that cover the polynomials up to a certain order with certain choices of α ; these are called “basis sets” and are given names like “6-31G*”, “TZ2P”, and “cc-pVQZ”. The general procedure is to pick one of these basis sets, and then to vary the C’s and the D’s to try to find an approximate $\Psi_{\text{electrons}}$ that solves the Schroedinger equation as closely as possible. If your basis set has a very good overlap with the true , you will be able to achieve good accuracy only varying a few C’s and D’s. If not,

There is a very nice variational theorem that says that you can compute the E corresponding to any approximate $\Psi_{\text{electrons}}$ by just evaluating a (very difficult multidimensional) integral, and that the one that returns the lowest E is best. So the problem is just to vary the C’s and D’s to minimize

$$E[\Psi] = E(C, D) = \langle \Psi_{\text{electrons}} | H_{\text{electrons}} | \Psi_{\text{electrons}} \rangle / \langle \Psi_{\text{electrons}} | \Psi_{\text{electrons}} \rangle$$

The evaluation of the integral requires $O(N_{\text{basis}}^3)$ operations. (Gaussian functions are used because they allow the integrals to be computed analytically.) Typically your basis set might include 15 atomic orbitals for each atom (except H atoms which doesn’t need so many) and you would vary the $(15 * N_{\text{atoms}})^2$ coefficients D_{mn} . The number of possible coefficients C is much larger, something like N_{basis} raised to the $N_{\text{electrons}}$ power, so it is almost always impossible to do anything with the complete expansion. Often people don’t bother to vary the C’s, or only allow a small fraction of the C’s to vary independently, to reduce the number of parameters. By allowing the C’s to vary, you are allowing to account for the fact that the different electrons are correlated with each other: when one is close to the nucleus the others are likely to be far away.

The fundamental problem is that we are trying to approximate a function of $3 * N_{\text{electrons}}$ variables. To beat this, people have come up with “Density Functional Theory (DFT)” where an approximate functional of the electron density (a function of only 3 variables) is used instead of a functional of the wavefunction Ψ . This functional intrinsically picks up

some of the largest contributions from electron correlation. In the most popular variety of DFT, you end up with equations that look almost the same as those but without any variable C's, so you just have to vary the D's to minimize the value of the functional:

$$E[\rho] = E(D)$$

DFT calculations are usually inexpensive; their accuracy is fundamentally limited by the fact that the $E[\rho]$ used is approximate. But with modern functionals they are pretty accurate (typical errors ~ 4 kcal/mole). Recently Kohn won the Nobel Prize for inventing DFT.

The approximations all have names, here is a **glossary**:

Semi-empirical (MOPAC, MNDO, AM1, PM3): vary the D's, but just use empirical estimates rather than the true integrals. Very cheap, but only accurate for molecule similar to those used to develop the empirical estimates.

DFT (B3LYP, BLYP, PW91): slightly empirical, but much more reliable than semi-empirical methods. CPU: cheap, same as HF $O(N^3)$. Errors ~ 4 kcal/mole (comparable accuracy to MP2 but much cheaper). Preferred method for geometries, second derivatives, first try at V(Ro).

HF (aka Hartree-Fock, SCF): only one C non-zero, vary the D's
CPU: cheap $O(N^3)$ errors ~ 15 kcal/mole

MP2, MP4 (aka Moller-Plesset, MBPT): Vary the D's first, then set the C's to the values given by perturbation theory (you don't freely vary these C's, saving CPU).
MP2: medium CPU: $O(N^5)$, errors ~ 5 kcal/mole

CI, CISD (Configuration Interaction): Vary the D's first, freeze them, then vary a lot of the C's.
Expensive. Not used much anymore, CCSD is preferred.

MCSCF, CASSCF: vary a finite set of C's and all the D's simultaneously.
Expensive. Good for understanding cases where several electronic states have comparable energies. User expertise required to select which C's to vary.

CAS-PT2: Determine the D's and some C's by CASSCF, then determine more C's by perturbation theory.
Not much more expensive than CASSCF. Sometimes very good, but not reliable.

MRCI (multi reference CI): Determine the D's and some C's by CASSCF or MCSCF, freeze these, then allow many of the C's to vary.
Super expensive. Very high accuracy for small systems.

CCSD, CCSD(T), QCISD (Coupled Cluster): Vary the D's, fix them, then vary a lot of the C's, but constraining certain relationships between the C's. This allows you to effectively use a longer expansion without increasing the number of adjustable parameters so much. The constraints force the solution to be "size-consistent", i.e. two molecules calculated simultaneously have exactly the same energy as two molecules calculated separately.

Expensive. Often very accurate.

Extrapolations ("Composite Methods"): G2, G3, CBS-q, CBS-Q, CBS-QB3, CBS-RAD

Run a series of the above calculations with different size basis sets, following some recipe. The results from all these calculations are extrapolated to an estimate of the true V(R). These methods give excellent accuracy in less CPU time than CCSD or MRCI. However, the multiple steps involved provide many opportunities for something to go wrong. Currently my favorite method is CBS-QB3, but I am waiting eagerly for the next generation of CBS methods to come out of Petersson's group at Wesleyan.

Accuracy: usually 1-2 kcal/mole

Notation

Method1/basis set 1 // method2/ basis set 2

This means "I computed the geometry using method 2 and basis set 2, and then I computed the energy at this geometry using method 1 and basis set 1." If there is no explanation, the second derivative calculations also come from method 2 using basis set 2.

When you explain what you have done, you must always specify both the method (e.g. B3LYP, MP2, CCSD(T)) and the basis set used. This is enough information that anyone else in the world should be able to repeat your calculation and get exactly the same results.

Isodesmic reactions

As you can see, there are many approximations in these calculations which cause the results to differ from experiment, and the absolute energies computed are often seriously wrong. However, differences between similar molecules are computed much more accurately than the absolute energies. So if you want a good enthalpy for a species X, do it this way:

1) find a reaction $X+A = B+C$ where the enthalpies of A,B,C are well known, and where the reactants and products are very similar (e.g. same numbers of each type of chemical bond). The more similar you can make both sides of the reaction, the better accuracy you will get, ideally the heat of reaction will be zero.

2) Compute the energies at the equilibrium geometries of X,A,B,C using the same quantum chemical method and basis set. From this compute the theoretical ΔH_{rxn} .

$$3) \Delta H_f(X)_{isodesmic} = H_f(B)_{expt} + H_f(C)_{expt} - \Delta H_f(A)_{expt} - \Delta H_{rxn}^{theor}$$

Unfortunately, it is difficult to use the same approach to improve the accuracy of transition state energies, since you seldom have well-known systems to compare with.

Some Warnings

- 1) The optimization (SCF/HF/DFT/CASSCF/MRSCF) problem required to solve for the D's is nonlinear and has multiple solutions, only one of which is the one you want (usually you want the lowest energy solution). So you may end up converging to a wavefunction which is qualitatively incorrect, perhaps it corresponds to an electronically excited state. There are some tools in Gaussian to help you figure out if this has happened.
- 2) Most of the quantum chemistry methods have problems (convergence, accuracy) with systems where there are low-lying electronic states (close to the ground state). In these cases, sometimes the numbers computed are completely nuts, other times they are subtly wrong. This is particularly a problem for transition states and where there are several lone pair electrons in the system. If you must study these systems, get expert assistance.
- 3) Many molecules have multiple geometrical conformations (local minima in $V(R)$), and sometimes there are multiple saddle points that might be confused with the TS. Look at your structures, if they are not what you expected, investigate. Also, it is worth some effort to make sure your initial guess at the molecular geometry is quite good, otherwise the geometry-optimization algorithm may get lost and waste a lot of CPU time to no avail. If you are having troubles, you can constrain some of the coordinates to make things easier for the optimizer.
- 4) For radicals and other open-shell systems, compare your computed solutions $\langle S^2 \rangle$ with the theoretical value $S(S+1)$. If your number is way off, chances are you have other problems as well. Sometimes you can use "restricted" methods like ROHF and RMP2, or spin-projection methods to fix this "spin-contamination" problem.
- 5) Every method runs into problems sometimes, and sometimes they are quite subtle. It is a good idea to double check your calculation with another calculation done using a very different method. If they both agree you can be pretty confident that your result is real.