Ab Initio Implementation of Hartree-Fock Molecular Orbital Theory

The fundamental assumption of HF theory – each electron sees all of the others as an average field. Neglect of electron correlation can have profound chemical consequences when it comes to determining accurate wave functions and properties derived therefrom. However, HF theory, in spite of its fairly significant fundamental assumption, was adopted as useful in the ab initio philosophy because it provides a very well defined stepping stone on the way to more sophisticated theories (i.e., theories that come closer to accurate solution of the Schrödinger equation). An enormous amount of effort has been spent on developing mathematical and computational techniques to reach the HF limit – to solve the HF equations with the equivalent of an infinite basis set, with no additional approximations. If the HF limit is achieved, then the energy error associated with the HF approximation for a given system, the electron correlation energy E_{corr}, can be determined as

$$E_{corr} = E - E_{HF}$$

Along the way, it became clear that HF energies and other properties could be chemically useful.

Basis sets

The basis set is the set of mathematical functions from which the wave function is constructed. Each MO in HF theory is expressed as a linear combination of basis functions, the coefficients from which are determined from the iterative solution of HF SCF equations.

The full HF wave function is expressed as a Slater determinant formed from the individual occupied MOs. In principle, the HF limit is achieved by use of an infinite basis set, however, in practice, one cannot make use of an infinite basis set. Thus, much work has gone into identifying mathematical functions that allow wave functions to approach the HF limit arbitrarily closely in as efficient manner as possible. Three considerations to make this process efficient: (i) the number of two-electron integrals increases as N^4 – we need to keep the total number of basis functions to a minimum; (ii) it is useful to choose basis set functional forms that permit to evaluate the integrals in a computationally efficient fashion: a larger basis set can still represent a computational improvement over a smaller basis set if evaluation of the greater number of integrals can be carried out faster; (iii) the basis functions must be chosen to have a form that is useful in a chemical sense – the functions should have large amplitude in regions of space where the electron probability density (the wave function) is also large and vice versa.

Functional forms

Slater orbitals, STOs: $$\varphi(r,\theta,\phi;\varsigma,n,l,m) = \frac{(2\varsigma)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\varsigma r} Y_l^m(\theta,\phi)$$

are attractive because they closely resemble hydrogenic atomic orbitals. However, no analytical solution is available for the general two-electron integral when the basis functions are STOs.

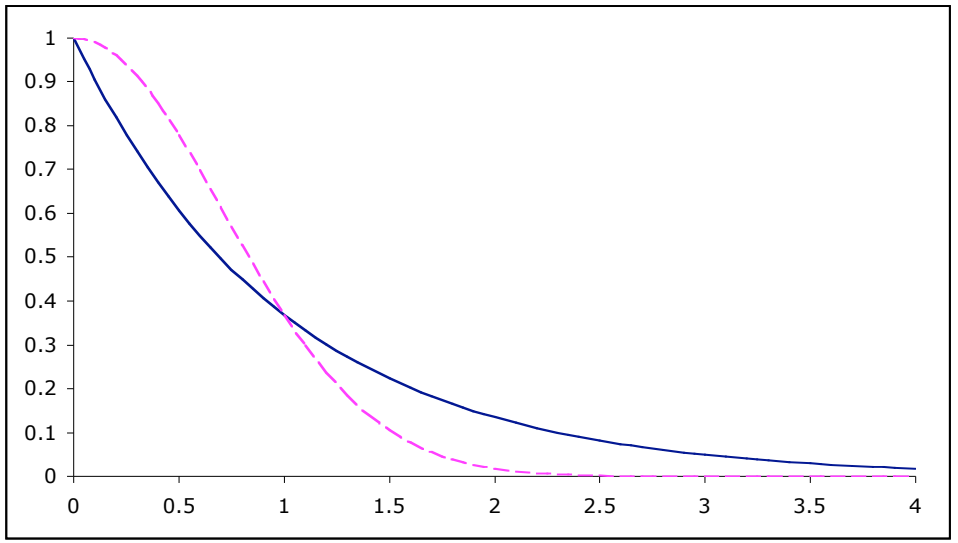
Boys (1950) proposed an alternative to the use of STOs. All that required for there to be an analytical solution of the general two-electron integral is that the radical decay of the STOs be changed from e^{-r} to e^{-r^2} - normalized Gaussian-type orbital (GTO) in atom-centered Cartesian coordinates:

$$\phi(x,y,z;\alpha,i,j,k) = \left(\frac{2\alpha}{\pi}\right)^{3/4}\left[\frac{(8\alpha)^{i+j+k} i!\, j!\, k!}{(2i)!(2j)!(2k)!}\right] x^i y^j z^k e^{-\alpha\left(x^2+y^2+z^2\right)}$$

$i = j = k = 0$ – GTO has spherical symmetry – s-type GTO
x ($i = 1, j = k = 0$), y ($j = 1, i = k = 0$), and z ($k = 1, i = j = 0$) – p-type GTOs (p_x, p_y, p_z); x^2, y^2, z^2, xy, xz, and yz – d-type GTOs

Contracted Gaussian Functions

Though convenient from a computational standpoint, GTOs have specific features that diminish their utility as basis functions – the shape of radial portion of the orbital. For s type functions, GTOs are smooth and differentiable at the nucleus ($r = 0$), but real hydrogenic AOs have a cusp. All hydrogenic AOs have a radial decay that is exponential in r while the decay of GTOs is exponential in r^2 – this results in too rapid a reduction in amplitude with distance for the GTOs.



In order to combine the best features of GTOs and STOs, one can use GTOs as building blocks to approximate STOs – linear combinations of GTOs fit to reproduce as accurately as possible a STO: $$\varphi(x,y,z;\{\alpha\},i,j,k) = \sum_{a=1}^{M} c_a \phi(x,y,z;\alpha_a,i,j,k)$$

When a basis function is defined as a linear combination of Gaussians – 'contracted' basis function; individual Gaussians – 'primitive' Gaussians. The degree of contraction' – *M*, the total number of primitives used to make all of the contracted functions. Contracted GTOs continue to permit analytical evaluation of all of the two-electron integrals. Hehre, Stewart, and Pople (1969) – systematically determined optimal contraction coefficients and exponents for mimicking STOs with contracted GTOs: M = 2-6 – STO-*M*G basis sets, 'Slater-Type Orbital approximated by *M* Gaussians'. The more primitives are employed, the more accurately a contracted function can be made to match a given STO, but the two-electron integral computation becomes increasingly complicated:

$$(\mu\nu \mid \lambda\sigma) = \int\int \varphi_\mu(1)\varphi_\nu(1)\frac{1}{r_{12}}\varphi_\lambda(2)\varphi_\sigma(2)dr_1 dr_2$$

$$= \sum_{a_\mu=1}^{M_\mu}\sum_{a_\nu=1}^{M_\nu}\sum_{a_\lambda=1}^{M_\lambda}\sum_{a_\sigma=1}^{M_\sigma} c_{a_\mu}c_{a_\nu}c_{a_\lambda}c_{a_\sigma}\int\int \phi_{a_\mu}(1)\phi_{a_\nu}(1)\frac{1}{r_{12}}\phi_{a_\lambda}(2)\phi_{a_\sigma}(2)dr_1 dr_2$$

The optimum combination of speed and accuracy – STO-3G. The old notation (3s)/[1s] (for H atom) is still used sometimes. In parentheses: the number and type of primitive functions; in brackets: the number and type of contracted functions.

For molecules containing H and first-row elements – notation is (6s3p/3s)/[2s1p/1s]. For higher rows than H and He, the exponents used for the primitive Gaussians in the s and p contractions can be the same (then the radial parts of all two-electron integrals are identical irresepective of whether they are (ss|ss), (ss|sp), (ss|pp), (sp|sp), etc.). The shapes of s- and p-type functions are different – the contraction coefficients are not identical. Such basis functions are called sometimes as sp basis functions.

Single-ζ, double-ζ, and split-valence basis sets

The STO-3G basis set is known as a 'single-ζ' or minimal basis set – one and only one basis function is defined for each type of core or valence orbital. For H and He, there is only a 1s function. For Li to Ne, there are five functions, 1s, 2s, $2p_x$, $2p_y$, and $2p_z$. For Na to Ar, 3s, $3p_x$, $3p_y$, and $3p_z$ are added to the second-row set (9 functions). This number is the absolute minimum required, nowhere near the infinite basis set limit.

One way to increase the flexibility of a basis set – to 'decontract' it. We may take the STO-3G basis set, and instead of constructing each basis function as a sum (linear combination) of three Gaussians, we could construct two basis functions for each AO, the first being a contraction of the first two primitive Gaussians and the second the normalized third primitive. This would not double the size of our basis set – we would have to evaluate all the same individual integrals as before – but the size of our secular equation would increase. A basis set with two functions for each AO – 'double-ζ' basis. We could decontract further and treat each primitive as a full-fledged basis function – a 'triple-ζ' basis, and we could then decide to add more functions indefinitely creating higher and higher multiple-ζ basis sets. These increasingly large basis sets must come closer and closer to the HF limit.

Valence orbitals can vary widely as a function of chemical bonding. Atoms bonded to significantly more electronegative elements take on partial positive charge from loss of valence electrons – their remaining density is distributed more compactly. The reverse is true when the bonding is to a more electropositive element. From a chemical standpoint, there is more to be gained by having flexibility in the valence basis functions than in the core – the development of 'split-valence' basis sets: core orbitals continue to be represented by a single (contracted) basis function but valence orbitals are split into arbitrarily many functions.

The most widely used split-valence basis sets (Pople's group): 3-21G, 6-31G, 6-311G. The first number indicates the number of primitives used in the contracted core functions. The numbers after the hyphen indicate the number of primitives used in the valence functions – if there are two such numbers, it is a valence-double-ζ basis, if there are three, valence-triple-ζ. How one should choose exponents and coefficients for the contracted functions? As the basis is no longer minimal, there is no particular advantage in fitting to STO. Pople and co-workers – use the variational principle. A test set of atoms and/or molecules was established, and exponents and coefficients were optimized so as to give the minimum energy over the test set. The name of a basis set refers to its contraction scheme and a list of all of its exponents and coefficients for each atom.

Modern basis sets – 'correlation-consistent' basis sets of Dunning: cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z – the exponents and contraction coefficients were variationally optimized not only for HF calculations, but also including electron correlation.

Polarization functions

We should remember about the distinction between atomic orbitals and basis functions in molecular calculations! Example: the inversion barrier for interconversion between equivalent pyramidal minima in NH_3 is 5.8 kcal/mol. However, a HF calculation with the equivalent of an infinite, atomic centered basis set of s and p functions predicts the geometry to be planar! The problem with the calculation is that s and p functions centered on the atoms do not provide sufficient mathematical flexibility to adequately describe the wave function for the pyramidal geometry, even though the atoms nitrogen and hydrogen can individually be reasonably well described entirely by s and p functions. The molecular orbitals, which are eigenfunctions of a Schrödinger equation involving multiple nuclei at various positions in space, require more mathematical flexibility than do the atoms. This flexibility is added in the form of basis functions with one quantum number higher angular momentum than the valence orbitals. A first-row atom – the most useful polarization functions are d GTOs, hydrogen – p GTOs. Adding d functions to the nitrogen basis set causes HF theory to predict correctly a pyramidal minimum for ammonia.

A variety of other molecular properties are sensitive to the presence of polarization functions: d functions on second-row atoms are absolutely required to make reasonable predictions for the geometries of molecules with hypervalent bonding situations: phosphates, sulfoxides, siliconates, etc.

6-31G* or 6-31G(d) – 6-31G basis set with a single set of d functions added to polarize the p functions. A second star imples p functions on H and He: 6-31G** or 6-31G(d,p).

There is a rough correspondence between the value of adding polarization functions and the value of decontracting the valence basis functions – there is a rough equality between each decontraction step and adding one new set of higher angular momentum: a balanced' double-ζ basis set should include d functions on heavy atoms and p functions on H, triple-ζ basis set should include 1 set of f functions and 2 sets of d functions on heavy atoms, and 1 set of d and 2 sets of p functions on H, etc. This is adopted in Dunning's cc-pV*n*Z basis sets. cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z

cc-pV6Z – each heavy atom has one I function, two h functions, three g functions, four f functions, five d functions, and six valence s and p functions, in addition to core functions – 140 basis functions for a single second-row atom.

6-31G(3d2fg,2pd) – heavy atoms are polarized by three sets of d functions, two sets of f functions, and a set of g functions, and H atoms by two sets of p functions and one of d.

Diffuse functions

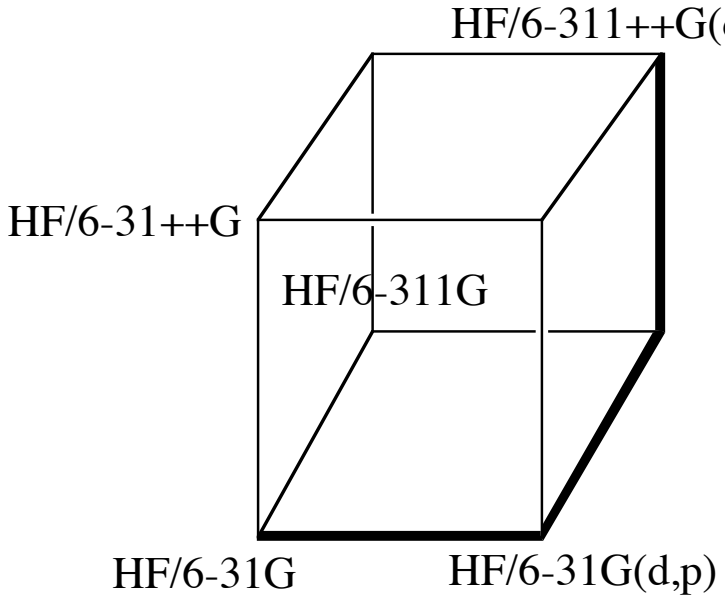
The highest energy MOs of anions, highly excited electronic states, and loose supermolecular complexes tend to be much more spatially diffuse than usual MOs. When a basis set does not have the flexibility to allow a weakly bound electron to localize far from the remaining density – significant errors in energies and other molecular properties can occur – standard basis sets are often augmented with diffuse basis functions: 6-31+G(d), 6-31++G(d,p), aug-cc-pV*n*Z. Particularly for the calculations of acidities and electron affinities, diffuse functions are absolutely required: the acidity of HF increases by 44 kcal/mol when 6-31+G(d) is used instead 6-31G(d).

The HF limit

Solution of the HF equations with an infinite basis set – the HF limit. Sometimes one can extrapolate to the HF limit. The c-pV*n*Z basis sets were designed for this purpose. As they increase with *n*, one can plot some particular computed property as a function of n^{-1} and extrapolate a curve fit back to the intercept – the intercept corresponds to $n = \infty$ - the infinite basis set limit. The cost of extrapolation becomes very large for $n = 4$, 5, and 6 – practical only for small systems (up to 5-6 atoms).

An alternative (more practical way): the assumption is made that the effects of 'orthogonal' increases in basis set size can be considered as additive. Consider HF calculations carried out for the following basis sets: 6-31G, 6-31++G, 6-31G(d,p), 6-311G, and 6-311++G(d,p). The additivity assumption is

$$E[\text{HF/6-311++G(d,p)}] \approx E[\text{HF/6-31G}] + \{E[\text{HF/6-31G(d,p)}] - E[\text{HF/6-31G}]\} + \{E[\text{HF/6-311G(d,p)}] - E[\text{HF/6-31G}]\} + \{E[\text{HF/6-31++G}] - E[\text{HF/6-31G}]\}$$



Effective core potentials

Very heavy elements pose a challenge for MO theory – they have large numbers of electrons – a large number of basis functions are required to describe them. These extra electrons are mostly core electrons. A radical solution for this problem – replace the electrons with analytical functions that would reasonably accurately, and much more efficiently, represent the combined nuclear-electronic core to the remaining electrons. Effective core potentials (ECPs) or pseudopotentials. In ab initio theory, ECPs represent not only Coulomb repulsion effects and adherence to the Pauli principle (atomic orbitals must be orthogonal to core orbitals having the same angular momentum).

The core electrons in very heavy elements reach velocities near the speed of light – they manifest relativistic effects. A non-relativistic Hamiltonian is incapable to account for such effects, which can be significant to many chemical properties. As an ECP represents the behavior of an atomic core, relativistic effects can be included in it.

How many electrons to include in the core? 'Large-core' ECPs include everything but the outermost (valence) shell; 'small-core' ECPs exclude the next lower shell. Polarization of the sub-valence shell can be chemically important in heavier metals – it is usually worth the extra cost to explicitly include that shell in the calculations. The most robust ECPs for the elements Sc-Zn, Y-Cd, and La-Hg employ [Ne], [Ar], and [Kr] cores, respectively.

Symmetry

The presence of symmetry in a molecule can be used to great advantage in electronic structure calculations and the advantages of symmetry are primarily associated with computational efficiency. The most obvious advantage – in geometry optimization. The presence of symmetry elements removes some of the $3N - 6$ degrees of molecular freedom. Consider C_6H_6 (benzene) as an example. 12 atoms – 30 degrees of freedom. If we restrict ourselves to D_{6h} symmetry – only two degrees of freedom (C-C and C-H bond lengths or *O*-C and *O*-H distances, where *O* is the center of the benzene ring). Symmetry is also very useful in several aspects of solving the SCF equations - it simplifies evaluation of one- and two-electron integrals and also reduces the dimension of the secular equation, as diagonalization of a block diagonal matrix can be accomplished by separate diagonalization of each block.

Sometimes symmetry is not employed deliberately. Why? This reflects a reluctance to work on a reduced dimensionality PES because minima on that PES may not be minima on the full PES. However, the best way to evaluate the nature of a stationary point, irrespective it was located using symmetry or not, is to carry out a calculation of the full-dimensional Hessian matrix and inspect the number of negative diagonal force constants (eigenvalues): all force constants are positive – local minimum; one is negative – transition state, etc. Higher symmetry calculations are more efficient in any case – impose symmetry at the start, release it if the number of negative eigenvalues in Hessian is not correct. Symmetry constraints must arise from molecular symmetry, not an erroneous idea of local symmetry. For example, the three C-H bonds of a methyl group should not be constrained to have the same length unless they are truly symmetrically related by a molecular threefold symmetry axis.

Efficiency of implementation and use

Formally, HF theory scales as N^4, where N is the number of basis functions. However, in practice, the situation is rarely so severe, and even linear scaling HF implementations have begun to appear. The first issue in implementation – how to calculate the two-electron integrals efficiently. The most straightforward way – to compute every single integral and, as it is computed, write it to storage – then, as Fock matrix is assembled element by element, call back the computed values whenever they are required (most of the integrals are required several times). In practice, this approach is useful only when the time required to write to read from storage is very fast. Otherwise, modern processors can recomputed the integral from scratch faster than modern hardware can recover the previously computed value from disk storage.

The process of computing each integral as it is needed – 'direct SCF'. Only when the storage of all integrals can be accomplished in memory itself (not on an external storage device), the access time is sufficiently fast and the 'traditional' method is preferable over direct SCF. As the size of the system increases – it is possible to estimate upper bounds for two-electron integrals efficiently. If the upper bound is negligibly small – there is no point to evaluate it and it is assigned to be zero. There are a lot of very small integrals in large systems, which can be neglected, so the scaling of HF theory improves. Fast-multipole methods can be also used to reduce the scaling of Coulomb integral evaluation.

Efficiency in converging the SCF for systems with large basis sets can be enhanced by using as an initial guess the converged wave function from a calculation with a smaller basis set or with a less negative charge. The same can be applied to geometry optimization – it is often very helpful to optimize the geometry first at a more efficient level of theory. This is true not only because the geometry optimized with the lower level is a good place to start for the higher level, but also because one can compute the force constants at the lower level and use them as an initial guess for the higher level Hessian matrix.

Taking advantage of molecular symmetry can provide very large savings in time. However, structures optimized under the constraints of symmetry should always be checked by computation of force constants to verify their nature as stationary points on the full PES. Also, it is worthwhile to verify that open-shell wave functions for symmetric molecules are stable with respect to orbital changes that would generate other electronic states. Finally, the use of ECP basis sets for heavy elements improves efficiency by reducing the scale of electronic structure problem and relativistic effects can be also accounted for.

General Performance Overview of Ab Initio HF Theory

Energetics

HF ignores correlation and, because in its ab initio formulation (as opposed to semiempirical), no attempts is made to correct for this deficiency, HF theory cannot realistically be used to compute heats of formation. Examination of the atomization energies of 66 small molecules at the HF level using the aug-cc-pV*n*Z basis sets gave mean absolute errors of 85, 66, and 62 kcal/mol with n = D, T, and Q, respectively.

Thus, even as one approaches the HF limit, the intrinsic error in an absolute molecular energy calculation can be very large. In general, the energy associated with any process involving a change in the total number of paired electrons is very poorly predicted at the HF level because electron correlation is not accounted for. Even if the number of paired electrons does not change but the nature of the bonds is substantially changed, the HF level can show large errors. Example: the atmospheric CO + OH $\rightarrow$ CO_2 + H reaction is known to be exoergic with the energy change of -23 kcal/mol. The HF level of theory using the STO-3G, 3-21G, 6-31G(d,p), and near-infinite quality basis sets predicts energy changes of +34.1, +3.1, -5.8, and –7.6 kcal/mol, respectively.

Isomerization is a process that can change bonding substantially as well. A comparison of experimental data with HF predictions at the HF/STO-3G, HF/3-21G, and HF/6-31G(d)//HF/3-21G levels was reported for 35 isomerization reactions. The isomerizations were quite diverse, with the energy differences from 0.2 to 62.6 kcal/mol. The mean absolute errors – 12.3, 4.8, and 3.2 kcal/mol at the three levels of theory, respectively. However, the maximum errors were 51.2, 22.6, and 11.3 kcal/mol – average performances are no guarantee of good behavior in any one system.

For comparison, MNDO, AM1, and PM3 calculations for the same set had mean absolute errors of 9.1, 7.4, and 5.8 kcal/mol, and maximal errors of 42, 24, and 23 kcal/mol.

The situation improves for conformational changes: 35 different conformational energy differences in organic molecules with the average energy difference between conformers of 1.6 kcal/mol – at the HF/6-31+G(d,p)//HF/6-31G(d) level, the RMS error in predicted differences was 0.6 kcal/mol. The simplest of conformational changes – rotation about a single bond. For eight rotations about H_mX-YH_n single bonds (X, Y = B, C, N, O, Si, S, P), Hehre et al. found mean absolute errors of 0.6, 0.6, and 0.3 kcal/mol at the HF/STO-3G, HF/3-21G*, and HF/6-31G* levels, respectively.

Although HF theory poorly computes most reaction energies, because of the substantial electron correlation effects due to making/breaking bonds, it is reasonably accurate for predicting protonation/deprotonation energies. The proton carries with it no electrons – these reactions are less sensitive to differential electron correlation in reactants and products. If basis sets of polarized valence-double-ζ quality or better are used, absolute proton affinities of neutral molecules typically have accuracy of better than 5%. Errors increase if the cations are non-classical (with bridging protons) – such structure tend to be found as minima only after accounting for electron correlation effects. Deprotonation energies of neutral compounds are computed with similar absolute accuracy ($\pm$8 kcal/mol) if diffuse functions are included in the basis set to balance the description of the anion. Otherwise, very large errors can occur.

Another fairly conservative reaction – the removal or attachment of a single electron from/to a molecule. Koopmans' theorem – the energy of the HOMO equals to the negative of IP.

This approximation ignores the effect of electronic relaxation in the ionized product – the degree to which the remaining electrons redistribute themselves following the detachment of one from the HOMO. Alternatively, we can calculate the IP as the difference in HF energies for the closed-shell neutral and the open-shell product, so-called ΔSCF IP:

$$IP_{\Delta SCF} = E_{HF}(A^{+\bullet}) - E_{HF}(A)$$

Here, orbital relaxation is included. Including relaxation results in a smaller predicted IP because relaxation lowers the energy of the cation radical relative to the neutral. However, we have to remember that the neutral species has one more electron and therefore there will be larger electron correlation effect. Ignoring these effects by employing HF theory, we destabilize the neutral more than the radical cation and the IP will be underestimated. Thus, Koopmans' theorem benefits from a cancellation of errors: the orbital relaxation and the electron correlation effects may cancel each other. In practice, the cancellation can be remarkably good; Koopmans' theorem IPs are often within 0.3 eV or so of experiment if basis sets of polarized valence-double-ζ quality or better are used in the HF calculation.

Koopmans' theorem can be formally applied to electron affinities (EAs) as well – the EA can be taken to be the orbital energy of the lowest unoccupied (virtual) orbital (LUMO). In this case, however, relaxation and correlation effects both favor the radical anion; rather than canceling, the errors are additive, and Koopmans' theorem estimates will almost always underestimate the EA. It is generally better to compute EAs from a ΔSCF approach whenever possible.

Can we use HF theory to model systems where two or more molecules are in contact, held together by non-bonded interactions? Such interactions include electrostatic interactions between permanent and induced charge distributions, dispersion, and hydrogen bonding.

HF theory is formally incapable of modeling dispersion because it is entirely a consequence of electron correlation. Nevertheless, bimolecular interaction energies are often reasonably well predicted by HF theory with basis sets like 6-31G(d) or similar – this again reflects a cancellation of errors. Failure to account for dispersion – strongly reduces intermolecular interactions, so the remaining errors must be in the direction of overbinding. Two main contributions to overbinding: (i) HF charge distributions tend to be overpolarized, which increases electrostatic interactions; (ii) a technical effect called 'basis set superposition error' (BSSE). If we consider a bimolecular interaction, the HF interaction energy is

$$\Delta E_{\text{bind}} = E_{HF}^{a\cup b}(A \bullet B) - E_{HF}^{a}(A) - E_{HF}^{b}(B)$$

If a and b are not both infinite basis sets, there are more basis functions employed in the calculation of the complex than in either of the monomers. The greater flexibility of the basis set for the complex can provide an artificial lowering of the energy when one of the monomers 'borrows' basis functions of the other to improve its own wave function. One method to correct for BSSE – counterpoise (CP) correction. The CP corrected interaction energy

$$E_{bind}^{CP} = E_{HF}^{a\cup b}(A \bullet B)_{A\bullet B} - E_{HF}^{a\cup b}(A)_{A\bullet B} - E_{HF}^{a\cup b}(B)_{A\bullet B} + \left[E_{HF}^{a}(A)_{A\bullet B} - E_{HF}^{a}(A)_{A}\right] + \left[E_{HF}^{b}(B)_{A\bullet B} - E_{HF}^{b}(B)_{A}\right]$$

The subscript after the molecular species describes the geometry employed. In the first line, the energy of bringing two monomers together, each monomer already having the geometry it has in the complex, is computed using a consistent basis set – in the monomer calculations, basis functions for the missing partner are included, even though the nuclei on which those functions are centered are not actually there (ghost basis functions).

The ghost functions lower the energies of the monomers – the overall binding energy is less. The second line – the energy required to distort each monomer from its preferred equilibrium structure to the structure found in the complex – the geometry distortion energies are computed using only the nuclei-centered monomer basis set.

The borrowing of basis functions in only partly a mathematical artifact. To the extent that some charge transfer and charge polarization indeed take place as part of forming the bimolecular complex, some of the borrowing simply reflects chemical reality. Thus, CP correction always overestimates BSSE.

Geometries

For minimum energy structures, HF geometries are usually very good when using basis sets of relatively modest size. For basis sets of polarized valence-double-ζ quality, errors in bond lengths between heavy atoms average about 0.03 Å, and between heavy atoms and H about 0.015 Å. Bond angles are predicted to an average accuracy of about 1.5º and dihedral angles are also generally well predicted.

Where we expect errors? HF theory tends to overemphasize occupation of bonding orbitals – errors tend to be in the direction of predicting bonds to be too short, and this effect becomes more pronounced as the basis set increases – the quality of HF calculations of geometry may actually degrade with basis set improvement. Polarization functions are absolutely required for geometric accuracy in systems with hypervalent bonding. In systems crowding many pairs of non-bonding electrons into small regions of space (four oxygen lone pairs in a peroxide) electron correlation effects on geometries can be large – HF geometries may not be reliable.

Dative bonds (those where both electrons in the bonding pair formally come from only one of the atoms) are often poorly described at the HF level. Example – B-C and B-N distances in the complexes H_3B-CO and H_3B-NH_3 are overestimated by ~0.1 Å at the HF/6-31G* level.

In the case of transition states (TSs), the failure of HF theory to account for electron correlation can be more problematic, since correlation effects in partial bonds can be large. Non-bonded complexes – the failure of HF theory to account for dispersion tends to make such complexes too loose in structure – intermolecular distances are unrealistically large. Hydrogen bonded structures are often quite good because errors in overestimating electrostatic interactions cancel the failure to account for dispersion.

Charge distributions

HF dipole moments are usually insensitive to increases in basis set size beyond valence-double-ζ. A systematic error in dipole moment – overestimation by 10-25%, molecules are predicted to be too polar. 108 molecules were examined at the HF/6-31G(d,p) level and a mean absolute error was 0.23 D. Results are erratic with smaller basis sets, in part due to lower quality wave functions and in part due to poorer geometries, which affect the dipole moment.