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Solving the HF equations I

The Fock equations are one-electron equations:

$$f|\chi_i\rangle = \epsilon_i |\chi_i\rangle$$

So we solve them using principles we have already developed for one-electron systems: introduce an expansion in a basis.

$$\chi_i(r) = \sum_m c_{im} \phi_m(r)$$

This leads to the set of linear equations:

$$\mathbf{Fc} = \epsilon \mathbf{Sc} \tag{1}$$

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which we can solve to find the energies and eigenfunctions. The question now is: how do we choose the basis functions $\{\phi_m\}$?



Slater-type orbitals I

A reasonable choice for basis sets for finite systems would be what are called Slater-type orbitals: these are very like solutions of the 1-electron Hamiltonian. They differ in two ways: (1) the radial part is simpler and (2) the exponent is not integral but can be varied to account for *screening* effects.

$$\phi = R_{nl}(r)\mathcal{Y}_{lm}(\theta,\phi) \tag{2}$$

where $\mathcal{Y}_{\textit{lm}}$ is a (real) spherical harmonic and the radial part is given by

$$R_{nl}(r) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r}$$
(3)



Slater-type orbitals II



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Slater-type orbitals III

Comments on Slater-type orbitals:

• GOOD Nuclear cusp condition satisfied.

$$\left. rac{\partial}{\partial r} \langle
ho(r)
angle_{\mathrm{sph}}
ight|_{r=0} = -2 Z \langle
ho(0)
angle_{\mathrm{sph}}$$

• GOOD Exact wavefunction has the long-range form of a Slater orbital.

If we pull one electron out of an $N\mbox{-electron}$ molecule the wavefunction behaves like

$$\Psi(N)
ightarrow \Psi(N-1) imes e^{-\sqrt{2*I}r}$$

where I is the first (vertical) ionization energy.

• BAD Integrals very difficult for multi-atom systems.



Gaussian-type orbitals (GTOs) I

In 1950 S. F. Boys pointed out that the problem of computing integrals could be resolved by using not Slater-type orbitals, but rather Gaussian-type orbitals (GTOs):

$$R_{nl} \sim r^l \mathrm{e}^{-lpha_n (r-\mathbf{A}_n)^2}$$

where **A** is the centre of the GTO. The main reason for the efficacy of GTOs is that the product of two GTOs is a third GTO, centred at a point in between:

$$\exp(-\alpha(r-\mathbf{A})^2)\exp(-\beta(r-\mathbf{B})^2) = \exp(-\gamma(\mathbf{A}-\mathbf{B})^2)\exp(-\mu(r-\mathbf{P})^2)$$

where $\mu = \alpha + \beta$, $\gamma = \alpha \beta / \mu$ and $\mathbf{P} = (\alpha \mathbf{A} + \beta \mathbf{B}) / \mu$.

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Gaussian-type orbitals (GTOs) II





Gaussian-type orbitals (GTOs) III

The general form of a GTO is

$$\psi_{\alpha_{nl}lm}^{\text{GTO}} = R_{l\alpha_n}^{\text{GTO}}(r) Y_{lm}(\theta, \phi)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics, and the radial part is given by

$$R_{l\alpha_n}^{\text{GTO}}(r) = \frac{2(2\alpha_n)^{3/4}}{\pi^{1/4}} \sqrt{\frac{2^{\prime}}{(2^{\prime}+1)!!}} (\sqrt{2\alpha_n}r)^{\prime} \exp\left(-\alpha_n(r-\mathbf{A}_n)^2\right)$$

The spherical harmonics are usually re-written as real solid harmonics to avoid complex algebra.

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Gaussian-type orbitals (GTOs) IV

- Notice that unlike the Slater-type orbitals, the *n*-dependence of a GTO lies in the choice of the exponent α_{nl} .
- The core orbitals with n = 0, 1 will be represented with relatively large exponents so that these orbitals decay quickly with r.
- Likewise, the valence orbitals with large *n* will be described with GTOs with small exponents so that they decay slowly.



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Gaussian-type orbitals (GTOs) V

- GOOD GTOs makes the integrals that appear in the HF energy expression much simpler.
- BAD Nuclear cusp condition violated: zero derivative at origin.
- BAD Wrong long-range form: dies off too fast with distance.

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Gaussian-type orbitals (GTOs) VI

Consider a GTO representation of the hydrogen 1s orbital: $1{\bf s_A}(r)=\pi^{-1/2}\exp{(-r)}.$

- No expansion in GTOs will ever be able to reproduce the cusp at r = 0.
- Likewise, any GTO expansion will decay with r much too fast.
- A single GTO does an incredibly poor job at describing $1 {\bf s_A}(r) ...$

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Gaussian-type orbitals (GTOs) VII



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Gaussian-type orbitals (GTOs) VIII



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Gaussian-type orbitals (GTOs) IX



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Gaussian-type orbitals (GTOs) X

We can do better using **contractions** In a contraction an orbital is defined as a *fixed* linear combination of GTOs.

$$\psi_{nlm}^{\rm cont} = \sum_{k \equiv (nl)} c_k \psi_{\alpha_k lm}^{\rm GTO}$$

where c_k are the contraction coefficients and α_k are the exponents of the GTOs in the contraction.

- The contraction coefficients can be chosen to ensure that the contraction is normalized, but this is not always the case.
- The c_k and the α_k are determined by fitting to reference energies or properties. The STO basis sets are designed to best approximate the Hartree–Fock energy of the atom.

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Gaussian-type orbitals (GTOs) XI

- Once determined these parameters are fixed.
- Hence a contraction significantly reduces the size of the basis while resulting in better energies.
- However, a basis must contain uncontracted GTOs too as these allow for orbitals deformation when bonds are formed.
- Hence basis sets consist of groups of contractions together with some un-contracted GTOs. The better the basis, the more of these there will be and the more GTOs in a contraction.

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Gaussian-type orbitals (GTOs) XII

cc-pvDZ Dunning basis for hydrogen:

h	сс	—pVDZ : [2s1p]	
	S	4	
	1	13.0100000	0.0196850000
	2	1.9620000	0.1379770000
	3	0.4446000	0.4781480000
	4	0.1220000	0.5012400000
	S	1	
	1	0.1220000	1.0000000000
	Р	1	
	1	0.7270000	1.000000000

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Gaussian-type orbitals (GTOs) XIII



Gaussian-type orbitals (GTOs) XIV





Gaussian-type orbitals (GTOs) XV

Clearly, the three contracted GTOs in the STO-3G basis do a much better job at describing the $1s_A(r)$ orbital of the hydrogen atom.

The cc-pVDZ basis for hydrogen contains a *p*-orbital in additionQ: to the two *s* orbitals. What is the purpose of this *p* orbitals?Also, since hydrogen has only one electron, why bother with an extra *s* orbital?

- We typically refer to a basis set by the number of orbitals it has in each symmetry. For example, the cc-pVDZ hydrogen basis is a 2s1p basis set.
- The better the basis the more the GTOs in a contraction and the more the number of GTOs of each symmetry.



Gaussian-type orbitals (GTOs) XVI

- Basis sets for each atom need to be matched: you cannot use a small carbon basis with a large hydrogen basis. Q: Why not?
- A set of matching basis sets will typically contain a similar number of functions on each atom in a given row of the periodic table. Allowances are made for the increasing number of shells as we go down the rows. So the cc-pVDZ Dumming basis set has: H:2s1p, C:3s2p1d, O:3s2p1d, Ar:4s3p1d. Notice how argon gets an extra *s* and *p* set.
- Commonly used families of basis sets are the Pople basis sets (typically used by chemists) and the Dunning basis sets (essential for correlated methods).



Gaussian-type orbitals (GTOs) XVII

- The Dunning basis sets go by the name (aug-)cc-p(C)VnZ. These are termed (augmented-)correlation-consistentpolarized-(contracted)-valence-n - ζ basis sets. The optional aug- refers to a set of extra diffuse GTOs that can be included to better describe response properties like the polarizability and hyperpolarizability.
- We typically think of these basis sets as a sequence that converges systematically to the **complete basis set** (CBS) limit.

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cc-pVDZ < cc-pVTZ < cc-pVQZ < ... < CBS
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• Ideally, we would always work at the CBS limit.

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Gaussian-type orbitals (GTOs) XVIII

Basis set recommendations:

- GOOD Complete basis set (CBS) limit
- Geometry optimization: moderate size basis sets. Double- ζ .
- Energies: At least triple- ζ quality.
- Properties: Triple- ζ or more.

We will have another look at basis sets after discussion correlated methods.

BSSE

BSSE I

Basis-set superposition error (BSSE) is an error encountered when using finite (incomplete) basis sets to calculate energy differences. First a few words about energy differences: we now know how to calculate molecular energies within the Hartree-Fock approximation. But energies on their own are almost meaningless: what is much more useful are differences in energy such as ionisation energies, or binding energies. We usually want to know what happens when, say, a complex forms. What is the energy gained or lost? Is it a stable or unstable process? (No thermodynamics here; we are at 0K) An important process is the formation of a complex. This is associated with an *interaction energy* defined as

 $E_{int}(\mathbf{R}, \Omega) = \mathbf{E}[\mathbf{A} \cdots \mathbf{B}](\mathbf{R}, \Omega) - \mathbf{E}[\mathbf{A}] - \mathbf{E}[\mathbf{B}],$

BSSE •••••

BSSE II

where E[A] and E[B] are the energies of the isolated monomers and $E[A \cdots B](R)$ is the energy of the complex in which the monomers are separated by R and rotated by Ω .

We need three energy calculations to compute an interaction energy and though it appears to be a straightforward calculation, we will generally get too large an interaction energy and the results with increasingly large basis sets do not always converge smoothly. The problem is largest with van der Waals complexes such as Ar_2 and Ne_2 . See the following figure for the latter complex:

BSSE III



Fig. 8.24. The interaction energy of the neon dimer (in μE_h) plotted as a function of the internuclear separation (in a_0). On the left, we have plotted the interaction energies calculated at the Hartree–Fock level in a complete basis (full line) and using the d-aug-cc-pVZZ sets with $X \le 4$ (with the number of consecutive dots indicating the cardinal number). No counterpoise correction has been applied to any of the Hartree–Fock curves. On the right, we have plotted the (counterpoise-corrected) interaction energies for different *ab initio* models at the frozen-core d-aug-cc-pVZZ level: the Hartree–Fock model (full line), the MP2 model (longer dashes), the CCSD model (shorter dashes) and the CCSD(T) model (dots). The thick grey line represents the potential-energy curve extracted from experiment [29].

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BSSE IV

All figures from: Molecular Electronic Structure Theory by Helgaker et al..

In the left panel the HF interaction energy is plotted with a variety of basis sets. There should be no binding at the HF level as this is a van der Waals complex and in such complexes all the binding arises from electron correclation that results in the van der Waals dispersion interaction. Yet, both the d-aug-cc-pVDZ and d-aug-cc-pVTZ basis sets result in binding! Even the d-aug-cc-pVQZ basis shows some binding at the HF level. The solid black line is what we should get. This error is termed the basis set superposition error or BSSE.

BSSE V



SNOOP, Kristensen et al. (2015)

The problem can be understood as follows: When we calculate the energy of the complex we use the basis space of both monomers. However, when we calculate the energy of the monomers, we have only the basis space of each individual monomer available. Therefore, for a variational method (and usually also for other



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methods), the energies of the monomers will be too high compared with the energy of the complex, resulting in too large an interaction energy.



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BSSE VII

SNOOP, Kristensen et al. (2015)

A solution is to calculate the monomer energies using the full basis of the dimer. This results in the counterpoise-corrected (CP) energies. Another solution is to calculate the energy of A using its own basis and the *virtual* space of B, and vice versa, for B. The latter approaches are termed VCP (virtual CP), and, in a very new development, the SNOOP (same number of optimised parameters) approach of Kristensen *et al.* (to appear in 2015).