Hartree-Fock Theory

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Many electron basis I

The many-electron basis has two requirements:

- Spin: We need to consider spin-orbitals rather than just spatial orbitals.
- Antisymmetry: The many electron basis functions cannot simply be products of one-electron spin-orbitals. It must be antisymmetric with respect to electron exchange.

Many electron basis II

The first condition is simple enough to take care of. If we have a spatial orbital $\psi(r)$ we can construct two spin-orbitals:

$$\chi(x) = \begin{cases} \psi(r)\alpha(\omega) \\ \psi(r)\beta(\omega) \end{cases}$$

All wavefunctions will be constructed from these spin-orbitals. We have assumed that there is no difference between the up and down spins states. This *restricted* solution is valid for a closed-shell systems. In general we will want to allow the spatial parts of the two spins to vary independently. This leads to what's known as an *unrestricted* solution. More later.

Many electron basis III

The antisymmetry condition puts restrictions on the kinds of trial wavefunctions we can use. Consider a two-electron case: The following trial wavefunction is not allowed for electrons

$$\Psi^{\mathrm{HP}}(x_1, x_2) = \chi_i(x_1)\chi_j(x_2)$$

This is because $\Psi^{\mathrm{HP}}(x_1, x_2) = \Psi^{\mathrm{HP}}(x_2, x_1)$. I.e., the wavefunction remains invariant on interchanging the electron labels. Such a wavefunction is suitable for bosons and is called the Hartree product (hence, the 'HP' superscript).

Many electron basis IV

To make our trial wavefunction antisymmetric we need it to be of the form:

$$\begin{aligned}\Psi(x_1, x_2) &= \frac{1}{\sqrt{2}}\left(\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)\right)\\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_i(x_1) & \chi_j(x_1)\\ \chi_i(x_2) & \chi_j(x_2)\end{vmatrix}\end{aligned}$$

This is called a *Slater determinant*.

Many electron basis V

More generally, for N-electrons the Slater determinant takes the form

$$\Psi(x_1, x_2, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \tag{1}$$

$$\equiv |\chi_i \chi_j \cdots \chi_k\rangle \tag{2}$$

where the last equation is short-hand for writing out the determinant.

Hartree–Fock (in brief) I

So now let us describe the ground state of our N-electron system with the BO approximation using a single Slater determinant:

$$\Psi_0(x_1, x_2, \cdots, x_N) = |\chi_1 \chi_2 \cdots \chi_N\rangle$$

The Hartree–Fock approximation to the ground state energy is found by varying the spin-orbitals $\{\chi_i\}$ to minimize the energy:

$$E_0 \leq E^{\mathrm{HF}} = \min \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$$

subject to the conditions that the spin-orbitals are orthonormal.

Hartree–Fock (in brief) II

As before, but with many more steps, the variational principle leads to the following equations for the spin-orbitals

$$f(i)\chi(x_i) = \epsilon\chi(x_i)$$

where $f(i)$ is an effective operator called the *Fock operator*

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}} + v^{\mathrm{HF}}(i)$$

where $v^{\mathrm{HF}}(i)$ is the Hartree–Fock *effective* potential that depends on the solutions to the above equations. So we must solve these equations self-consistently: Make a guess for the solutions; construct the potential $v^{\mathrm{HF}}(i)$ from this guess; solve the Fock equations; get new solutions; and repeat till convergence.

One-electron operators I

We will require a number of matrix elements for Hartree–Fock and post-HF methods. You have already seen these when we worked through the H_2 system. The rules for general N-electron matrix elements are very similar to those for the 2-electron case; the only complication is the added complication brought out by the algebric complexity of the N-electron Slater determinants.

Szabo & Ostlund describes the calculation of these matrix elements in some detail and I expect you to look through those derivations in case the ones presented here are not clear enough for you. A problem with the S&O derivations is that they are too long. More on this soon.

One-electron operators II

We are after matrix elements of the form

$$\langle K|\mathcal{O}_1|L\rangle \quad \text{and} \quad \langle K|\mathcal{O}_2|L\rangle$$

where $|K/L\rangle$ are N-electron Slater determinant wavefunctions. In general, the N-electron determinant $|\Psi\rangle$ can be written as

$$|\Psi\rangle = (N!)^{-1/2} \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$$

Here $\mathcal{P}_u$ is a permutation operator that can be expressed as a product of binary permutations:

$$\mathcal{P}_u = \mathcal{P}_{ij}\mathcal{P}_{kl}\cdots$$

and σ_u is phase factor that is $+1$ if $\mathcal{P}_u$ contains an even number of binary permutations and is -1 otherwise.

One-electron operators III

We now define the antisymmetrization operator $\mathcal{A}$ as

$$\mathcal{A} = \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u$$

Recall that the Hartree product (HP) is defined as $\Psi^{\mathrm{HP}} = \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$, so we will often write $|\Psi\rangle$ more compactly as

$$|\Psi\rangle = (N!)^{-1/2}\mathcal{A}\Psi^{\mathrm{HP}}.$$

The operator $\mathcal{A}$ is Hermitian so $\mathcal{A} = \mathcal{A}^\dagger$ and

$$\mathcal{A}\mathcal{A} = N!\mathcal{A}.$$

One-electron operators IV

These properties allow us to significantly simplify matrix element evaluation, for consider

$$\langle \Psi | H | \Psi \rangle = (N!)^{-1} \sum_{u=1}^{N!} \sigma_u \sum_{w=1}^{N!} \sigma_w \times \int dx_1 \cdots dx_N$$
$$\mathcal{P}_u \{ \chi_1(1) \chi_2(2) \cdots \chi_N(N) \} \; H \; \mathcal{P}_w \{ \chi_1(1) \chi_2(2) \cdots \chi_N(N) \}$$

Handling two permutation operators is tedious. S&O do it and you should see how these proofs go, but we will use the following theorem to make the proofs significantly easier:

One-electron operators V

Theorem

$$\langle \Psi | H | \Phi \rangle = \sqrt{N!}\ \langle \Psi^{HP} | H | \Phi \rangle .$$

Proof:

$$\begin{aligned}
\langle \Psi | H | \Phi \rangle &= \langle \mathcal{A}\Psi^{\mathrm{HP}} | H | \mathcal{A}\Phi^{\mathrm{HP}} \rangle \\
&= (N!)^{-1}\ \langle \Psi^{\mathrm{HP}} | H | \mathcal{A}\mathcal{A}\Phi^{\mathrm{HP}} \rangle \\
&= (N!)^{-1}\ \langle \Psi^{\mathrm{HP}} | H | N!\mathcal{A}\Phi^{\mathrm{HP}} \rangle \\
&= \langle \Psi^{\mathrm{HP}} | H | \mathcal{A}\Phi^{\mathrm{HP}} \rangle \\
&= \sqrt{N!}\ \langle \Psi^{\mathrm{HP}} | H | \Phi \rangle
\end{aligned}$$

One-electron operators VI

Using the above theorem we can write

$$\langle\Psi|H|\Psi\rangle = \int dx_1 \cdots dx_N$$

$$\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}\ H\ \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}$$

There is only one permutation operator to deal with here.
Now we will consider a series of cases with the operator being: C (a C-number), $\sum_i h(i)$, and $\sum_{i>j} r_{ij}^{-1}$. Additionally, we will consider matrix elements involving Ψ and singly and doubly excited determinants: Ψ_i^a and Ψ_{ij}^{ab}. We will not consider higher excitations as the rules for those follow from these.

One-electron operators VII

C: C-number

$$\langle\Psi|C|\Psi\rangle =$$

$$C\langle\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}|\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}\rangle$$

- $\mathcal{P}_u = E$: we get $C\langle 1|1\rangle\langle 2|2\rangle\cdots = C$.
- $\mathcal{P}_u = \mathcal{P}_{12}$: we get $-C\langle 1|2\rangle\langle 1|2\rangle\langle 3|3\rangle\cdots = 0$.
- Similarly for other permutations.

Therefore, $\langle\Psi|C|\Psi\rangle = C$. Which also means that $|\Psi\rangle$ as defined is normalized!

One-electron operators VIII

$\sum_\mathbf{i} \mathbf{h(i)}$: One-electron operator
Consider $h(i)$ only:

$\langle \Psi | h(i) | \Psi \rangle =$

$$\langle \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\} | h(i) | \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u \{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\} \rangle$$

- $\mathcal{P}_u = E$: $\langle 1|1\rangle \cdots \langle i|h(i)|i\rangle \cdots = \langle i|h|i\rangle$.
- $\mathcal{P}_u = \mathcal{P}_{ij}$: $-\langle 1|1\rangle \cdots \langle i|h(i)|j\rangle \cdots \langle j|i\rangle \cdots = 0$.
- Similarly, any other permutation gives a 0.

Therefore, $\langle \Psi | h(i) | \Psi \rangle = \langle i|h|i\rangle$, and

$$\langle \Psi | \sum_i h(i) | \Psi \rangle = \sum_i \langle i|h|i\rangle = \sum_i h_{ii}.$$

One-electron operators IX

$\sum_{\mathbf{i>j}} \mathbf{r}_{\mathbf{ij}}^{-\mathbf{1}}$: two-electron operator

Consider r_{ij}^{-1} only:

$$\langle\Psi|r_{ij}^{-1}|\Psi\rangle =$$

$$\langle\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}|r_{ij}^{-1}|\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1(1)\chi_2(2)\cdots\chi_N(N)\}\rangle$$

- $\mathcal{P}_u = E$: $\langle 1|1\rangle\cdots\langle i(i)j(j)|r_{ij}^{-1}|i(i)j(j)\rangle\cdots = (ii|jj)$.
- $\mathcal{P}_u = \mathcal{P}_{ij}$: $-\langle 1|1\rangle\cdots\langle i(i)j(j)|r_{ij}^{-1}|i(j)j(i)\rangle\cdots = -(ij|ji)$.
- Any other permutation gives a 0.

Therefore, $\langle\Psi|r_{ij}^{-1}|\Psi\rangle = (ii|jj) - (ij|ji)$, and

$$\langle\Psi|\sum_{i>j} r_{ij}^{-1}|\Psi\rangle = \sum_{i>j}[(ii|jj) - (ij|ji)].$$

One-electron operators X

Putting these results together we can now write down the energy expression of any single-determinant wavefunction $|\Psi\rangle$:

$$\boxed{\langle\Psi|H|\Psi\rangle = \sum_{i}\langle i|h|i\rangle + \sum_{i>j}[(ii|jj) - (ij|ji)]}$$

One-electron operators XI

Singly excited states: $\Psi_i^a = (N!)^{-1/2}\mathcal{A}\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\}$

$$\langle \Psi_i^a | h | \Psi \rangle =$$

$$\langle \{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\} | h | \sum_{u=1}^{N!} \sigma_u \mathcal{P}_u \{\chi_1 \cdots \chi_{i-1}\chi_i\chi_{i+1}\cdots\}\rangle$$

Contributions from $h = \sum_j h(j)$ must eliminate the zero overlap term $\langle \chi_a | \chi_i \rangle$. The only term that can do this is $h(i)$. Now consider the cases:

- $\mathcal{P}_u = E$: $\langle 1|1\rangle \cdots \langle a(i)|h(i)|i(i)\rangle \cdots = \langle a|h|i\rangle = h_{ai}$.
- $\mathcal{P}_u = \mathcal{P}_{ij}$: $-\langle 1|1\rangle \cdots \langle a(i)|h(i)|j(i)\rangle \cdots \langle j(j)|i(j)\rangle \cdots = 0$.
- All other permutations result in a 0.

Therefore $\langle \Psi_i^a | h | \Psi \rangle = \langle a|h|i\rangle = h_{ai}$.

One-electron operators XII

Singly excited states: $\Psi_i^a = (N!)^{-1/2}\mathcal{A}\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\}$

$$\langle\Psi_i^a|\sum_{kl} r_{kl}^{-1}|\Psi\rangle =$$

$$\langle\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1}\cdots\}|\sum_{kl} r_{kl}^{-1}|\sum_{u=1}^{N!}\sigma_u\mathcal{P}_u\{\chi_1 \cdots \chi_{i-1}\chi_i\chi_{i+1}\cdots\}\rangle$$

Once again, to eliminate the zero overlap term $\langle\chi_a|\chi_i\rangle$ we must have either $k = i$ or $l = i$. It doesn't matter which as these are dummy variables. So let us choose $k = i$ and $l = j$ (j goes over all electrons). We have effectively made the replacement: $\sum_{kl} r_{kl}^{-1} \rightarrow \sum_j r_{ij}^{-1}$.

One-electron operators XIII

- $\mathcal{P}_u = E$:

$$\langle \{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1} \cdots \chi_j \cdots\}|\sum_j \frac{1}{r_{ij}}|\{\chi_1 \cdots \chi_{i-1}\chi_i\chi_{i+1} \cdots \chi_j \cdots\}\rangle$$

$$= \sum_j \langle \chi_a(i)\chi_j(j)|r_{ij}^{-1}|\chi_i(i)\chi_j(j)\rangle \equiv \sum_j \langle aj|ij\rangle = \sum_j (ai|jj)$$

- $\mathcal{P}_u = \mathcal{P}_{ij}$:

$$-\langle \{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1} \cdots \chi_j \cdots\}|\sum_j \frac{1}{r_{ij}}|\{\chi_1 \cdots \chi_{i-1}\chi_j\chi_{i+1} \cdots \chi_i \cdots$$

$$= -\sum_j \langle \chi_a(i)\chi_j(j)|r_{ij}^{-1}|\chi_j(i)\chi_i(j)\rangle \equiv -\sum_j \langle aj|ji\rangle = -\sum_j (aj|ji)$$

One-electron operators XIV

- All other permutations — those that do not involve i — will result in a 0. Show it!

So we have the result:

$$\boxed{\langle \Psi_i^a | \sum_{kl} \frac{1}{r_{kl}} | \Psi \rangle = \sum_j [(ai|jj) - (aj|ji)]}$$

And, including the one-electron terms, we have:

$$\boxed{\langle \Psi_i^a | H | \Psi \rangle = \langle a|h|i \rangle + \sum_j [(ai|jj) - (aj|ji)]}$$

One-electron operators XV

Doubly excited states:

$$\Psi_{ij}^{ab} = (N!)^{-1/2}\mathcal{A}\{\chi_1 \cdots \chi_{i-1}\chi_a\chi_{i+1} \cdots \chi_{j-1}\chi_b\chi_{j+1} \cdots\}$$

Q: Show that

- There are no contributions from the one-electron operator $h = \sum_i h(i)$.
- The two-electron operator $\sum_{kl} \frac{1}{r_{kl}}$ results in single contribution: $(ai|bj) - (aj|bi)$. No summations here.

Consequently,

$$\langle\Psi_{ij}^{ab}|\sum_{kl} \frac{1}{r_{kl}}|\Psi\rangle = (ai|bj) - (aj|bi)$$

One-electron operators XVI

This time there is no contribution from the one-electron part, so

$$\boxed{\langle\Psi_{ij}^{ab}|H|\Psi\rangle = (ai|bj) - (aj|bi)}$$

Introduction I

We now know that the energy of a single determinant $|\Psi\rangle$ can be written as

$$\langle\Psi|H|\Psi\rangle = \sum_i \langle i|h|i\rangle + \sum_{i>j}[(ii|jj) - (ij|ji)]$$

The problem here is that we still do not know what the spin-orbitals (SOs) χ_i are or how to calculate them. As we shall see, the variational principle comes to our aid and allows us to re-cast this result as an eigenvalue equation. More importantly, it will turn out to be a *one-electron* eigenvalue equation of the form

$$\hat{f}|\chi_m\rangle = \epsilon_m|\chi_m\rangle.$$

Introduction II

We will show that the one-electron Fock operator $\hat{f}$ is defined as

$$f(1) = h(1) + v^{\mathrm{HF}}(1),$$

where $h(1)$ is the usual one-electon Hamiltonian and v^{HF} is the Hartree–Fock effective potential that is defined as follows:

$$v^{\mathrm{HF}}(1) = \sum_i [\mathcal{J}_i(1) - \mathcal{K}_i(1)],$$

where the Coulomb and exchange operators are defined as

$$\mathcal{J}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}}\right] \chi_m(1)$$

$$\mathcal{K}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_m(2)}{r_{12}}\right] \chi_i(1)$$

Introduction III

Have a look at the form of the Coulomb operator:

$$\mathcal{J}_i(1) = \int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}} = \int dx_2 \frac{\rho_i(2)}{r_12}.$$

This is the Coulomb potential of the electron in orbital χ_i. So in the expression

$$\mathcal{J}_i(1)\chi_m(1) = \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_i(2)}{r_{12}}\right] \chi_m(1)$$

electron 1 in orbital χ_i does not see the potential from a point electron at 2, but rather, interacts with this electron via the classical Coulomb potential arising from the electronic density.

Introduction IV

Of course, this is a quantum system, so we also have an exchange interaction. Unlike the Coulomb interaction, this one has a complex form: the exchange operator includes the orbital on which it is operating.

$$\begin{aligned}\mathcal{K}_i(1)\chi_m(1) &= \left[\int dx_2 \frac{\chi_i^*(2)\ \chi_m(2)}{r_{12}}\right]\chi_i(1) \\ &= \left[\int dx_2 \frac{\chi_i^*(2)\ \mathcal{P}_{12}\ \chi_i(2)}{r_{12}}\right]\chi_m(1)\end{aligned}$$

where, in the second form, we have used the permutation operator $\mathcal{P}_{12}$ to perform the exchange. This also allows us to write the operator $\mathcal{K}_i$ in more conventional form.

Introduction V

Because the electrons do not interact directly with other electrons, but rather, see the average potential (Coulomb and exchange) from other electrons, Hartree–Fock theory is called a *mean-field theory*. Here is the Fock Hamiltonian again:

$$\boxed{f(1) = h(1) + \sum_i \int dx_2 \frac{\chi_i^*(2)\,(1-\mathcal{P}_{12})\,\chi_i(2)}{r_{12}}}$$

We will now prove this and demonstrate the the SOs χ_a are eigenstates of this Fock operator. (They are not eigenstates of the Hamiltonian $\mathcal{H}$!)

Derivation I

We need to minimize

$$E_0[\{\chi_i\}] = \langle\Psi|H|\Psi\rangle = \sum_i \langle i|h|i\rangle + \sum_{i>j}[(ii|jj) - (ij|ji)]$$

w.r.t. the $\{\chi_i\}$ subject to the conditions $\langle\chi_i|\chi_j\rangle = \delta_{ij}$. The orthonormality condition can be included using the method of Lagrange multipliers, i.e., we minimize the functional

$$\mathcal{L}[\{\chi_i\}] = E_0[\{\chi_i\}] - \sum_{ij}^{N} \epsilon_{ji} \left(\langle\chi_i|\chi_j\rangle - \delta_{ij}\right)$$

Derivation II

First a result we will need:

Q: All terms in the functional $\mathcal{L}$ are real. Use this fact to show that $\epsilon_{ji} = \epsilon_{ij}^*$.

Hint: Set $s_{ij} = \langle \chi_i | \chi_j \rangle - \delta_{ij}$ and consider the real sum $\sum_{ij} \epsilon_{ji} s_{ij}$. Use the fact that $s_{ij} = s_{ji}^*$ to show the required result.

Derivation III

For an extremum, under the variation $\chi_i \to \chi_i + \delta\chi_i$ we must have

$$0 = \delta\mathcal{L} = \delta E_0 - \sum_{ij} \epsilon_{ji} \delta\langle i|j\rangle$$

Consider the first term:

$$\begin{aligned} \delta E_0 = &\sum_i \{\langle \delta i|h|i\rangle + \langle i|h|\delta i\rangle\} \\ &+ \frac{1}{2}\sum_{ij}\{(\delta i i|jj) + (i\delta i|jj) + (ii|\delta j j) + (ii|j\delta j)\} \\ &- \frac{1}{2}\sum_{ij}\{(\delta i j|ji) + (i\delta j|ji) + (ij|\delta j i) + (ij|j\delta i)\} \end{aligned}$$

Derivation IV

Q: Using the symmetry relations $(ij|kl) = (kl|ij)$, $(ij|kl)^* = (ji|lk)$ and the fact that we can always rename the dummy indices i and j, show that

$$\sum_{ij}(ii|\delta jj) = \sum_{ij}(\delta ii|jj)$$

Similar results hold for the other terms.

Hence show that

$$\delta E_0 = \sum_i \langle \delta i|h|i\rangle + \sum_{ij}[(\delta ii|jj) - (\delta ij|ji)] + \text{c.c.}$$

Derivation V

Similarly, use the result $\epsilon_{ji} = \epsilon_{ij}^*$ to show that

$$\begin{aligned}\sum_{ij} \epsilon_{ji} \delta \langle i|j\rangle &= \sum_{ij} \epsilon_{ji} (\langle \delta i|j\rangle + \langle i|\delta j\rangle) \\ &= \sum_{ij} \epsilon_{ji} \langle \delta i|j\rangle + \text{c.c.}\end{aligned}$$

Putting this all together we get

$$0 = \delta \mathcal{L} = \sum_{i} \langle \delta i|h|i\rangle + \sum_{ij} [(\delta i i|jj) - (\delta i j|j i)] - \sum_{ij} \epsilon_{ji} \langle \delta i|j\rangle + \text{c.c.}$$

Derivation VI

Let's now write this out in terms of the Coulomb and exchange operators:

$$0 = \sum_i^N \int dx_1 \delta\chi_i^*(1) \times$$

$$\left[h(1)\chi_i(1) + \sum_j^N (\mathcal{J}_j(1) - \mathcal{K}_j(1))\chi_i(1) - \sum_j^N \epsilon_{ji}\chi_j(1) \right] + \text{c.c.}$$

Derivation VII

Since the variations $1\delta\chi_i^*(1)$ are arbitrary, we must have the quantities in the $[\cdots] = 0$. Hence,

$$\left(h(1) + \sum_j^N (\mathcal{J}_j(1) - \mathcal{K}_j(1)) \right) \chi_i(1) = \sum_j \epsilon_{ji} \chi_j(1)$$

or,

$$f|\chi_i\rangle = \sum_j \epsilon_{ji} |\chi_j\rangle$$

This is not yet in the form we want it to be. Let's now see how we can recast this equation to convert it into the standard *canonical* form.

Derivation VIII

There is a freedom in defining the orbitals $\{\chi_i\}$: the *occupied* SOs can be mixed amongst themselves without changing the energy. Let's see how this is so by defining a new set of SOs that are derived from the old set via a *unitary transformation*:

$$\chi'_i = \sum_j \chi_j U_{ji}$$

where $\mathbf{U}^\dagger = \mathbf{U}^{-1}$, i.e., $\mathbf{U}$ is unitary.
We now show that the Fock operator remains unchanged if we replace the $\{\chi_i\}$ orbitals by the s $\{\chi'_i\}$s.

Derivation IX

The one-electron operator $h = \sum_i h(i)$ is trivially unchanged as it doesn't depend on the SOs. Consider the Coulomb operator:

$$\begin{aligned}
\sum_i \mathcal{J}_i'(1) &= \sum_i \int dx_2 \frac{\chi_i'^*(2)\ \chi_i'(2)}{r_{12}} \\
&= \sum_{kl} [U_{ki}^* U_{li}] \int dx_2 \frac{\chi_k^*(2)\ \chi_l(2)}{r_{12}} \\
&= \sum_{kl} [\delta_{kl}] \int dx_2 \frac{\chi_k^*(2)\ \chi_l(2)}{r_{12}} \\
&= \sum_{k} \int dx_2 \frac{\chi_k^*(2)\ \chi_k(2)}{r_{12}} \\
&= \sum_i \mathcal{J}_i(2)
\end{aligned}$$

Derivation X

Here, the indices i, k, l all go over occupied orbitals only.

Index Notation:

- Occupied orbitals: i, j, k, l
  (S&O use a, b, c, d)
- Un-occupied/virtual orbitals: a, b, c, d
  (S&O use r, s, t, u)
- General orbitals: m, n, o, p

Remember that the Fock operator is defined in terms of the *occupied* orbitals but can *operate on* all orbitals.

Derivation XI

Q: Show that the exchange operator is also unchanged under a unitary transformation of the occupied orbitals. I.e. show that $\sum_i \mathcal{K}_i' = \sum_i \mathcal{K}_i$.

Hence we get our result: $f'(1) = f(1)$: the Fock operator is invarient under a unitrary transformation of the occupied SOs. Now, since

$$f|\chi_i\rangle = \sum_j \epsilon_{ji}|\chi_j\rangle$$

we have

$$\langle\chi_i|f|\chi_j\rangle = \sum_k^N \epsilon_{kj}\langle\chi_i|\chi_k\rangle = \epsilon_{ij}$$

Derivation XII

therefore

$$\begin{aligned}\epsilon'_{ij} &= \int dx_1 \chi_i'^*(1) f(1) \chi_j'(1) \\ &= \sum_{kl} U_{ki}^* U_{lj} \int dx_1 \chi_k^*(1) f(1) \chi_l(1) \\ &= \sum_{kl} U_{ki}^* \epsilon_{kl} U_{lj}\end{aligned}$$

So, in matrix form: $\epsilon' = \mathbf{U}^\dagger \epsilon \mathbf{U}$.
Now, we have shown that ϵ is an Hermitian matrix, so we can always find a Unitary matrix that diagonalises it. Let this matrix be **U**. Therefore, ϵ' will be a diagonal matrix. Hence

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

Derivation XIII

or, dropping the primes, we write the Fock equations in canonical form:

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

Notes:

- The canonical spin orbitals are generally delocalised.
- Like the non-canonical SOs, they are orthonormal.
- We have proved that we can obtain a set of canonical SOs for the occupied orbitals. It turns out that this can be done for the virtual (un-occupied) SOs too.

Orbital Energies I

What do the spin orbitals and orbitals energies mean? When we solve the Fock equations we formally obtain an infinity of solutions (any partial differential equation has an infinity of solutions). We place the N electrons in the N lowest energy SOs. These are our occupied orbitals. The others, the un-occupied ones, are called the virtual SOs. There are an infinity of these (formally!). We will now try to understand what these orbitals mean. But first, something to think about

Q: Why have we assumed (as we will) that the putting the electrons in the N lowest energy SOs is the correct thing to do? After all, our goal is to minimize the energy E_0 which, as we will soon see, is not the same as the sum of the energies of the occupied SOs.

Orbital Energies II

What are the orbital energies?

$$\begin{aligned}\epsilon_i &= \langle \chi_i | f | \chi_i \rangle = \langle \chi_i | h + \sum_j (\mathcal{J}_j - \mathcal{K}_j) | \chi_i \rangle \\ &= \langle \chi_i | h | \chi_i \rangle + \sum_j [\langle \chi_i | \mathcal{J}_b | \chi_i \rangle - \langle \chi_i | \mathcal{K}_b | \chi_i \rangle] \\ &= \langle i | h | i \rangle + \sum_j [\langle ij | ij \rangle - \langle ij | ji \rangle] \\ &= \langle i | h | i \rangle + \sum_j \langle ij || ij \rangle\end{aligned}$$

Orbital Energies III

Now let's look at the energies of an occupied and a virtual orbital:

- **Occupied orbital**

$$\epsilon_i = \langle i|h|i\rangle + \sum_j \langle ij||ij\rangle = \langle i|h|i\rangle + \sum_{j\neq i} \langle ij||ij\rangle$$

  We could eliminate the $j = i$ case in the sum as $\langle ii||ii\rangle = 0$. These is the way self-interaction is removed in Hartree–Fock theory. Notice that the sum now includes Coulomb and exchange interactions with $N - 1$ electrons.

- **Virtual orbital**

$$\epsilon_a = \langle a|h|a\rangle + \sum_j \langle aj||aj\rangle$$

  Since $j \in$ occ, we cannot make the same reduction in the sum and see that this electron in the virtual orbital a interacts with N other electrons.

Orbital Energies IV

Q: Do the orbital energies add up to the total energy?

$$\begin{aligned}\sum_i^N \epsilon_i &= \sum_i \langle i|h|i\rangle + \sum_{ij} \langle ij||ij\rangle \\ &= E_0 + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle\end{aligned}$$

So $E_0 \neq \sum_i^N \epsilon_i$! The reason for this difference is that, as we have jsut seen, ϵ_i includes the Coulomb and exchange interactions (in the average, HF sense) with the other $N-1$ electrons. So by summing over all ϵ_i we double count and hence to get E_0 we need to remove half these interactions.

Koopman's Theorem I

To find out exactly what these Hartree–Fock orbital energies mean we evaluate the Ionization Potential (IP) and Electron Affinity (EA) while keeping all orbitals frozen (no relaxation allowed).

The IP is defined as the energy taken to remove an electron. We will remove the electron from orbital k. This creates the $N-1$ electron state

$$|\Psi_k(N-1)\rangle = a_k|\Psi_0\rangle$$

And

$$\mathrm{IP} = E_k(N-1) - E_0(N)$$

where

$$\begin{aligned} E_0(N) &= \langle\Psi_0(N)|H|\Psi_0(N)\rangle \\ E_k(N-1) &= \langle\Psi_k(N-1)|H|\Psi_k(N-1)\rangle. \end{aligned}$$

Koopman's Theorem II

We already know that

$$E_0(N) = \sum_i \langle i|h|i\rangle + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

To evaluate $E_k(N-1)$ we use a similar expression but eliminate all instances of orbital k:

$$E_k(N-1) = \sum_{i\neq k}\langle i|h|i\rangle + \frac{1}{2}\sum_{i\neq k, j\neq k}\langle ij||ij\rangle$$

Koopman's Theorem III

So the IP is

$$\begin{aligned}
\mathrm{IP} &= E_k(N-1) - E_0(N) \\
&= -\langle k|h|k\rangle - \frac{1}{2}\sum_i \langle ik||ik\rangle - \frac{1}{2}\sum_j \langle kj||kj\rangle \\
&= -\langle k|h|k\rangle - \sum_i \langle ik||ik\rangle \\
&= -\epsilon_k
\end{aligned}$$

So the orbital energy ϵ_k of occupied orbital k is negative of the energy required to remove the electron from the orbital while keeping all orbitals fixed.

Koopman's Theorem IV

Now consider the process of adding an electron to a virtual orbital a of the system to generate $|\Psi^a(N+1)\rangle = a_a^\dagger|\Psi_0\rangle$. The electron affinity is defined as

$$\mathrm{EA} = E_0(N) - E^a(N+1).$$

Q: Show that

$$\mathrm{EA} = E_0(N) - E^a(N+1) = -\epsilon_a$$

That is, the energy of a virtual orbital is the negative of the electron affinity for adding an electron to that orbital.

Koopman's Theorem V

This now explains why an electron in a virtual orbital has an energies that is consistent with it interacting with N other electrons. From the above we see that this is so because the energy of a virtual orbital is (minus) the energy required to create an $N+1$ state.

Koopman's Theorem VI

Koopmans' Theorem

Given an N-electron Hartree–Fock single determinant with occupied and virtual spin orbital energues ϵ_i and ϵ_a, the ionization potential to produce an $N-1$-electron state with all orbitals frozen and the electron removed from orbital i is $-\epsilon_i$, and the electron affinity to produce a $N+1$-electron state with an additional electron in virtual orbital a is $-\epsilon_a$.

Brillioun's Theorem I

Brillioun's theorem deals with the *stability* of the Hartree–Fock solution w.r.t. first-order changes to the wavefunction (the Fock single-determinant).

We have derived the Fock equations using the variational principle, so, the solutions to the Fock equations should be stable in the variational sense, that is, the Hartree–Fock energy should not change (to first order) with small changes to the wavefunction.

What Brillioun's Theorem tells us is that this is indeed true if by *small changes* we mean *single excitations*: that is, single excitations will not change the Hartree–Fock energy.

Brillioun's Theorem II

To demonstrate this we need a couple of results:

$$\begin{aligned}\langle \Psi_i^a | H | \Psi_0 \rangle &= \langle a|h|i\rangle + \sum_j [(ai|jj) - (aj|ji)] \\ &= \langle a|h|i\rangle + \sum_j \langle aj||ij\rangle\end{aligned}$$

Brillioun's Theorem III

and we need the general form of matrix elements of the Fock operator:

$$\begin{aligned} f_{mn} = \langle \chi_m | f | \chi_n \rangle &= \langle \chi_m | h + \sum_j (\mathcal{J}_j - \mathcal{K}_j) | \chi_n \rangle \\ &= \langle \chi_m | h | \chi_n \rangle + \sum_j [\langle \chi_m | \mathcal{J}_b | \chi_n \rangle - \langle \chi_m | \mathcal{K}_b | \chi_n \rangle] \\ &= \langle m | h | n \rangle + \sum_j [\langle mj | nj \rangle - \langle mj | jn \rangle] \\ &= \langle m | h | n \rangle + \sum_j \langle mj || nj \rangle \end{aligned}$$

Brillioun's Theorem IV

Now, because the SOs χ_m are eigenstates of the Fock operator, we have

$$f_{mn} = \langle \chi_m | f | \chi_n \rangle = \epsilon_n \langle \chi_m | \chi_n \rangle = \epsilon_n \delta_{mn}.$$

From the second result we see that

$$\begin{aligned} \langle \Psi_i^a | H | \Psi_0 \rangle &= \langle a | h | i \rangle + \sum_j \langle aj || ij \rangle \\ &= \langle \chi_a | f | \chi_i \rangle \\ &= \epsilon_i \delta_{ai} = 0 \quad \text{since} \quad a \neq i \end{aligned}$$

That is, the singly excited determinant Ψ_i^a does not (directly) connect with the Hartree–Fock ground state Ψ_0.
To see the significance of this result, let us consider a CI expansion to *improve* the Hartree–Fock wavefunction and energy.

Brillioun's Theorem V

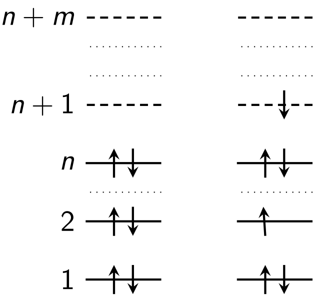


Figure : Left: HF ground state configuration. Right: An example of an excited state configuration. If there are n occupied levels (2 electrons each, so $N = 2n$) and m virtual (un-occupied) levels, in how many ways can we form excited states? Each of these states will correspond to a Slater determinant.

Brillioun's Theorem VI

We generate the full CI (FCI) wavefunction by including all kinds of single determinants in a linear expansion:

$$\begin{aligned}|\Psi\rangle &= c_0|\Psi_0\rangle + \sum_{ia} c_i^a|\Psi_i^a\rangle + \sum_{ij,ab} c_{ij}^{ab}|\Psi_{ij}^{ab}\rangle + \cdots \\ &= c_0|\Psi_0\rangle + c_S|S\rangle + c_D|D\rangle + \cdots\end{aligned}$$

where electrons are excited from the *occupied* orbitals $i, j, k, \cdots$ to the *virtual* orbitals $a, b, c, \cdots$.

We may think that the simplest way to improve the HF solution $|\Psi_0\rangle$ is to include the single excitations $|S\rangle$. This is a reasonable assumption that proves to be wrong because of Brillouin's theorem. To see this, consider the simple case where we have only

Brillioun's Theorem VII

one singly excited determinant $|\Psi_i^a\rangle$. So the CI — call it CIS for configuration interaction with single excitations — expansion is

$$|\Psi\rangle = |\Psi_0\rangle + c_i^a|\Psi_i^a\rangle$$

Using the usual variational methods we have discussed before to determine the coefficients c_0 and c_{ij}^{ab} we convert this problem into the set of linear equations

$$\begin{pmatrix} \langle\Psi_0|H|\Psi_0\rangle & \langle\Psi_0|H|\Psi_i^a\rangle \\ \langle\Psi_i^a|H|\Psi_0\rangle & \langle\Psi_i^a|H|\Psi_i^a\rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix} = \mathcal{E} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix}$$

From Brillouin's theorem $\langle\Psi_i^a|H|\Psi_0\rangle = 0$ and $\langle\Psi_0|H|\Psi_0\rangle = E_0$, therefore we get

$$\begin{pmatrix} E_0 & 0 \\ 0 & \langle\Psi_i^a|H|\Psi_i^a\rangle \end{pmatrix} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix} = \mathcal{E} \begin{pmatrix} c_0 \\ c_i^a \end{pmatrix}$$

Brillioun's Theorem VIII

The ground-state solution is simply $\mathcal{E} = E_0$ with $c_0 = 1$ and $c_i^a = 0$. I.e., the ground-state of the CIS variational expansion is the Hartree–Fock solution. That is, singly excited determinants (on their own) cannot improve the Hartree–Fock solution. I.e., Hartree–Fock is *stable* to perturbations that take the form of single excitations.

This does not mean that single excitation can never contribute. They can if we also include double excitations. Can you see how?

The HF Hamiltonian I

The HF single-determinant wavefunction is *not* an eigenstate of the Hamiltonian:

$$H|\Psi_0\rangle \neq E_0|\Psi_0\rangle.$$

But it is an exact eigenstate of the *Hartree–Fock Hamiltonian*

$$H_0 = \sum_i^N f(i)$$

Q: Show that it is. And show that the eigenvalue is $E_0^(0) = \sum_i \epsilon_i$.

The HF Hamiltonian II

Now we can write $H = H_0 + V$, where V is the *fluctuation operator* defined as

$$\begin{aligned} V &= H - H_0 \\ &= \sum_{i,j>i} \frac{1}{r_{ij}} - \sum_i v^{\mathrm{HF}}(i). \end{aligned}$$

That is, V is the difference in the exact two-electron interaction operator and the approximate HF operator.
We can treate V as a perturbation to H_0 and expand the energy as

$$\mathcal{E}_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \cdots$$

We will do this properly later when covering perturbation theory in detail, but for now, all we need are the first two terms. Recall from

The HF Hamiltonian III

your Quantum Mechanics that $E_0^{(0)} = \langle \Psi_0 | H_0 | \Psi_0 \rangle = \sum_i \epsilon_i$ and $E_0^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle$.

Q: Show that $E_0^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle = -\frac{1}{2} \sum_{ij} \langle ij || ij \rangle$

Hence we see that the Hartree–Fock energy is the sum of the first two terms in the perturbation theory expansion:

$$E_0 = E_0^{(0)} + E_0^{(1)} = \sum_i \epsilon_i - \frac{1}{2} \sum_{ij} \langle ij || ij \rangle.$$

Q: Show that this expression is exactly the same as the earlier one we derived for the Hartree–Fock energy.

Therefore, there is no first-order contribution to this perturbation theory. The first-order term is included in Hartree–Fock.

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:

$$\mathbf{Fc} = \epsilon\mathbf{Sc} \tag{3}$$

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

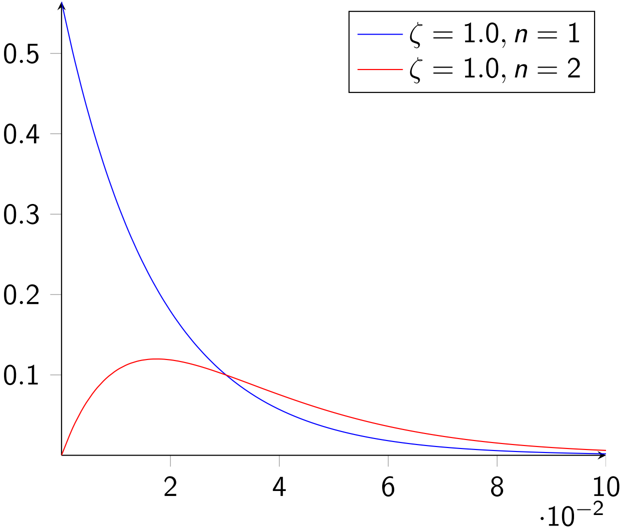
A reasonable choice for basis sets for finite systems would be what are called Slater-type orbitals: these are very like solutions of the 1-electron Hamiltonian. They differ in two ways: (1) the radial part is simpler and (2) the exponent is not integral but can be varied to account for *screening* effects.

$$\phi = R_{nl}(r)\mathcal{Y}_{lm}(\theta, \phi) \tag{4}$$

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

$$R_{nl}(r) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} \tag{5}$$

Slater-type orbitals II



Slater-type orbitals III

Comments on Slater-type orbitals:

- GOOD Nuclear cusp condition satisfied.

$$\frac{\partial}{\partial r}\langle\rho(r)\rangle_{\mathrm{sph}}\Big|_{r=0} = -2Z\langle\rho(0)\rangle_{\mathrm{sph}}$$

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

  If we pull one electron out of an N-electron molecule the wavefunction behaves like

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

  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):

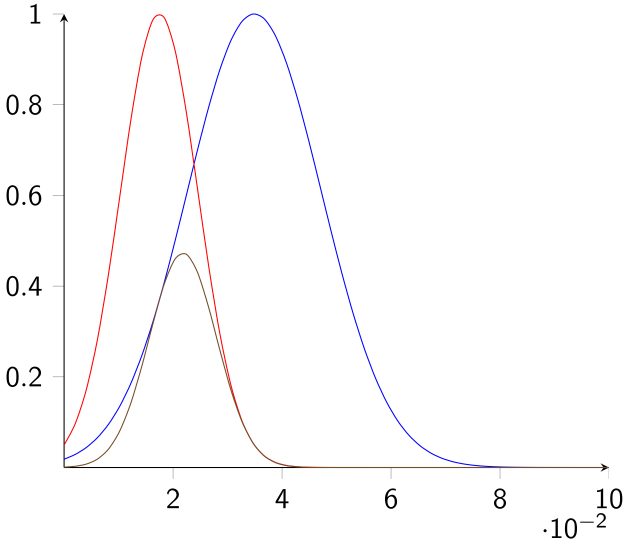
$$R_{nl} \sim r^n e^{-\alpha(r-\mathbf{A})^2}$$

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

Gaussian-type orbitals (GTOs) II



Gaussian-type orbitals (GTOs) III

The general form of a GTO is

$$\psi^{\mathrm{GTO}}_{\alpha_{nl}lm} = R^{\mathrm{GTO}}_{\alpha_{nl}l}(r)Y_{lm}(\theta,\phi)$$

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

$$R^{\mathrm{GTO}}_{\alpha_{nl}l}(r) = \frac{2(2\alpha_{nl})^{3/4}}{\pi^{1/4}}\sqrt{\frac{2^l}{(2l+1)!!}}(\sqrt{2\alpha_{nl}}r)^l \exp\left(-\alpha_{nl}r^2\right)$$

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

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.

Gaussian-type orbitals (GTOs) V

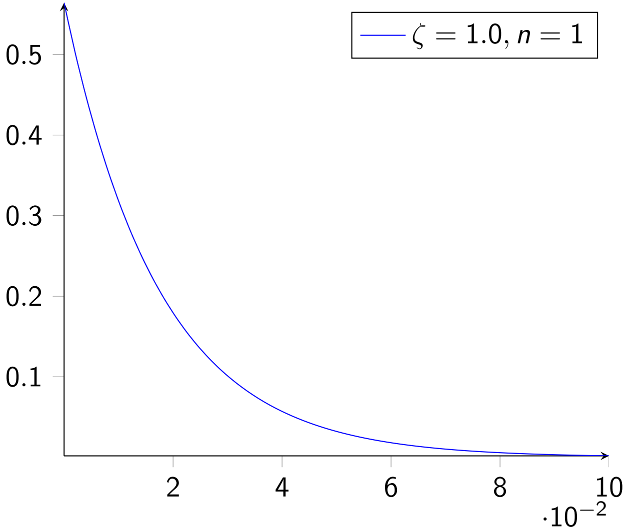
- GOOD GTOs makes the integrals that appear in the HF energy expression much simpler.
- BAD Nuclear cusp condition violated: zero derivative at origin.
- BAD Wrong long-range form: dies off too fast with distance.

Gaussian-type orbitals (GTOs) VI

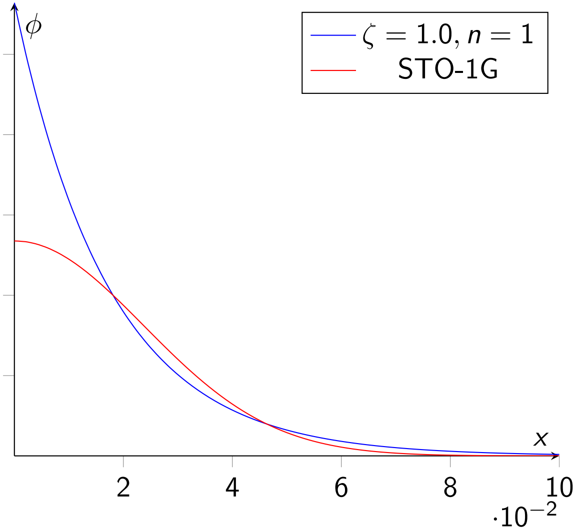
Consider a GTO representation of the hydrogen 1s orbital:
$1\mathbf{s_A}(\mathbf{r}) = \pi^{-1/2} \exp(-r)$.

- 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 $1\mathbf{s_A}(\mathbf{r})$...

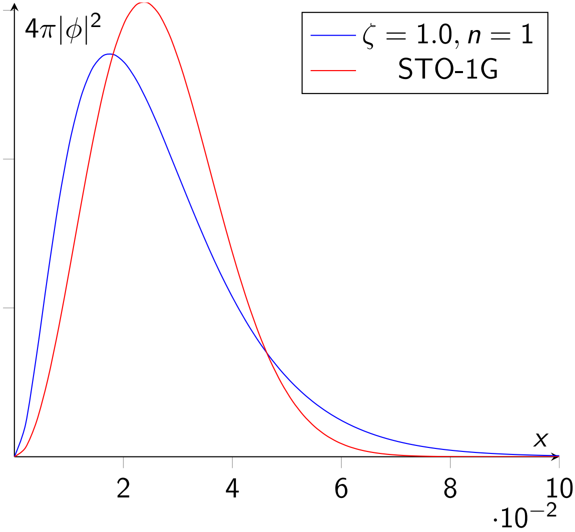
Gaussian-type orbitals (GTOs) VII



Gaussian-type orbitals (GTOs) VIII



Gaussian-type orbitals (GTOs) IX



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.

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

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.

Gaussian-type orbitals (GTOs) XI

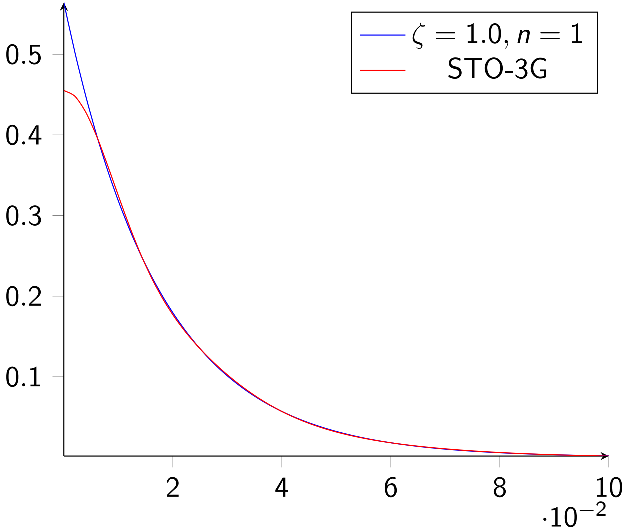
- Once determined these parameters are fixed.
- Hence a contraction significantly reduces the size of the basis while resulting in better energies.
- However, a basis must contain uncontracted GTOs too as these allow for orbitals deformation when bonds are formed.
- Hence basis sets consist of groups 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.

Gaussian-type orbitals (GTOs) XII

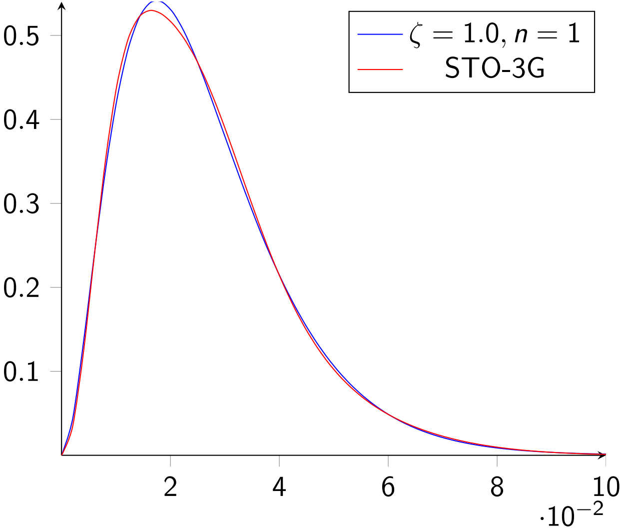
cc-pvDZ Dunning basis for hydrogen:

```
h       cc-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
        P     1
    1         0.7270000          1.0000000000
```

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 $1s_{\mathbf{A}}(\mathbf{r})$ orbital of the hydrogen atom.

Q: The `cc-pVDZ` basis for hydrogen contains a *p*-orbital in addition 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)V`*n*`Z`. These are termed (augmented-)correlation-consistent-polarized-(contracted)-valence-$n - \zeta$ 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.

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

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.