Ab initio methods: Post-Hartree-Fock

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Hartree–Fock equations I

We have introduced basis sets in solving the Hartree–Fock equations, but what exactly are they? Brief summary of Hartree–Fock theory:

- Born–Oppenheimer approximation: fixed nuclei.
- Ground-state *N*-electron wavefunction: single Slater determinant:

$$\Psi_0(x_1, x_2, \cdots, x_N) = |\chi_1 \chi_2 \cdots \chi_N\rangle \tag{1}$$

Variational Principle:

$$E_0 \leq E^{\mathrm{HF}} = \min \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$$
 (2)

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

Basis sets CI CC MBPT Summary
Hartree–Fock equations II

• Fock equations:

$$f(i)\chi(x_i) = \epsilon \chi(x_i) \tag{3}$$

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

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \mathbf{v}^{\mathrm{HF}}(i)$$
(4)

where $v^{\text{HF}}(i)$ is the Hartree–Fock *effective* potential.

- Self-consistent solution (iterations needed).
- Infinity of solutions to the Fock equations.
- Introduce a basis for the spatial part of spin-orbitals:

$$\chi_i(r) = \sum_m C_{im} \phi_m(r) \tag{5}$$

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Basis sets	CI	CC	MBPT	Summary
Hartree-Fo	ock equation	s III		

• Leads to linear equations:

$$\mathbf{FC} = \epsilon \mathbf{SC} \tag{6}$$

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Q: How do we choose the basis?



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.

$$\phi = R_{nl}(r)\mathcal{Y}_{lm}(\theta,\phi) \tag{7}$$

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

$$R_{nl}(r) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r}$$
(8)

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Basis sets	CI	CC	MBPT	Summary
Slater-type	orbitals II			



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Basis sets CI CC MBPT Summary
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

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

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):

$$R_{nl} \sim r^n e^{-\alpha (r-\mathbf{A})^2} \tag{9}$$

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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



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- 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.

The two negative points can, to some extent, be remedied by using not single GTOs, but *linear combinations* of GTOs. These groups of GTOs are termed *contractions*.

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) IV

cc-pvDZ Dunning basis for hydrogen:

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	1.000000000
Р	1	
1	0.7270000	1.000000000
	cc- S 1 2 3 4 5 1 P 1	cc-pVDZ : [2s1p] S 4 1 13.0100000 2 1.9620000 3 0.4446000 4 0.1220000 S 1 1 0.1220000 P 1 1 0.7270000

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 Basis sets
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 Gaussian-type orbitals (GTOs) V



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Gaussian-type orbitals (GTOs) VI



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Basis sets	CI	CC	MBPT	Summary

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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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.

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Basis sets	CI	СС	MBPT	Summary
Correlation I				

Q: How to we improve on the complete basis set HF results? I.e., how do we get beyond the HF limit?

• Variational Principle: More flexibility. Leads to Configuration Interaction (CI).

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- Perturbation Theory
- Coupled-cluster methods
- Density functional theory

Basis sets	CI	CC	MBPT	Summary
Configurat	tion Interacti	on I		

Cl: Increase the flexibility in the wavefunction by including in addition the the HF ground state, excited states. Q: What are excited states and how to we form them?

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Basis sets	CI	СС	MBPT	Summary
Configurati	on Interacti	on II		



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.

Basis sets	CI	CC	MBPT	Summary

Configuration Interaction III

The Full CI (FCI) wavefunction:

$$\begin{split} |\Psi\rangle &= |\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle + \sum_{abrs} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \cdots \\ &= |\Psi_0\rangle + c_S |S\rangle + c_D |D\rangle + \cdots \end{split}$$

where electrons are excited from the *occupied* orbitals a, b, c, \cdots to the *virtual* orbitals r, s, t, \cdots .

- GOOD This expansion will lead to the *exact* energy *within the basis set used*.
- BAD There are too many determinants!

 $\frac{(2(n+m))!}{(2n)!(2m)!}$

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 Basis sets
 CI
 CC
 MBPT
 Summary

 Configuration Interaction IV

One solution to the problem is to use only some of the many determinants. For example we could use only double excitations. This leads to the CID method.

$$egin{aligned} |\Psi^{ ext{CID}}
angle &= |\Psi_0
angle + \sum_{abrs} c^{rs}_{ab} \left|\Psi^{rs}_{ab}
ight
angle \ &= |\Psi_0
angle + c_D \left|D
ight
angle \end{aligned}$$

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BAD This theory, like all truncated CI methods, is not *size extensive*.

Size-extensivity: If E(N) is the energy of N non-interacting identical systems then a method is size-extensive if $E(N) = N \times E(1)$.

Configuration Interaction V

Q: Is CID size-extensive?

If $\hat{\mathcal{T}}_2$ is an operator that creates all double excitations, then we can write the CID wavefunction as

$$egin{aligned} \left| \Psi^{ ext{CID}}
ight
angle &= \left| \Psi_0
ight
angle + \sum_{abrs} c^{rs}_{ab} \left| \Psi^{rs}_{ab}
ight
angle \ &= \left| \Psi_0
ight
angle + c_D \left| D
ight
angle \ &= (1 + \hat{\mathcal{T}}_2) \left| \Psi_0
ight
angle \end{aligned}$$

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Basis sets CI CC MBPT Summary
Configuration Interaction VI

The CID wavefunction for each of two identical non-interacting systems will be of that form, so the combined wavefunction will be

$$\begin{split} \left| \Psi_A^{\text{CID}} \right\rangle \left| \Psi_B^{\text{CID}} \right\rangle &= \left(1 + \hat{T}_2(A) \right) \left| \Psi_0^A \right\rangle \left(1 + \hat{T}_2(B) \right) \left| \Psi_0^B \right\rangle \\ &= \left(1 + \hat{T}_2(A) + \hat{T}_2(B) + \hat{T}_2(A) \hat{T}_2(B) \right) \left| \Psi_0^A \right\rangle \left| \Psi_0^B \right\rangle \end{split}$$

The last excitation term is a quadruple excitation so it will not be present in the CID wavefunction for the combined A and B systems. Therefore

$$E^{\mathrm{CID}}(AB) \neq E^{\mathrm{CID}}(A) + E^{\mathrm{CID}}(B).$$

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Basis sets	CI	СС	MBPT	Summary
Configurati	on Interacti	ion VII		
Conngulati	on meracu			

CI is not size-extensive: H_2



Figure : An energy level diagram for H_2 with a minimal basis. The two MOs are as shown. We can form three determinants from them. Left is the ground state. Middle is a *singly excited* determinant. Right is a *doubly excited* determinant. For reasons of symmetry the middle configuration does not contribute to the CI expansion.

Basis sets	CI	CC	MBPT	Summary
CISD: Exar	nples I			



Fig. 11.1. The cc-pVDZ correlation energy per water monomer (as a percentage of the FCI correlation energy) as a function of the number of noninteracting water molecules. The grey line represents the FCI energy, the full black line the CISD energy, and the dotted line the CISD energy with the Davidson correction applied. The calculations have been carried out for the C_{2v} water molecule at the OH separations $R = R_{ref}$ (left) and $R = 2R_{ref}$ (right); see Table 11.2.

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

Basis sets	CI	CC	MBPT	Summary
CISD: Exan	nples II			



Fig. 11.2. The weight of the Hartree–Fock determinant in the FCI wave function (grey line) and in the CISD wave function (black line) as a function of the number of noninteracting water monomers in the cc-pVDZ basis. The plot on the left corresponds to the molecular equilibrium geometry; the plot on the right represents a situation where the OH bonds have been stretched to twice the equilibrium bond distance. For details on the calculations, see Table 11.2.

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Basis sets	CI	CC	MBPT	Summary
CISD: Exan	nnles III			



Fig. 11.3. The weights of the excitation levels in the FCI wave function for a system containing one to ten noninteracting water monomers. The plot on the left corresponds to the molecular equilibrium geometry in the cc-pVDZ basis; the plot on the right represents a situation where the OH bonds have been stretched to twice the equilibrium bond distance. For details on the calculations, see Table 11.2.

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Coupled-cluster Theory I

The problem of truncated CI methods is severe enough that using them is very problematic. A resolution to the problem is the class of coupled-cluster theories. In these the wavefunction is defined as:

$$\left|\Psi^{ ext{CC}}
ight
angle=\exp(\hat{ extsf{T}})\left|\Psi_{0}
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where \hat{T} is an appropriate excitation operator.

Basis sets CI CC MBPT Summary
Coupled-cluster Theory II

For example, in CCD theory we use \hat{T}_2 as the excitation operator. This gives:

$$egin{aligned} \left| \Psi^{ ext{CCD}}
ight
angle &= \exp(\hat{\mathcal{T}}_2) \left| \Psi_0
ight
angle \ &= \left(1 + \hat{\mathcal{T}}_2 + rac{1}{2!} \hat{\mathcal{T}}_2 \hat{\mathcal{T}}_2 + \cdots
ight) \left| \Psi_0
ight
angle \end{aligned}$$

The first two terms give us CID theory. The rest are needed to make CCD size-extensive:

$$\exp(\hat{T}_{2}(A)) \left| \Psi_{0}^{A} \right\rangle \times \exp(\hat{T}_{2}(B)) \left| \Psi_{0}^{B} \right\rangle = \exp(\hat{T}_{2}(A) + \hat{T}_{2}(B)) \left| \Psi_{0}^{A} \right\rangle \left| \Psi_{0}^{B} \right\rangle$$
$$\equiv \exp(\hat{T}_{2}(AB)) \left| \Psi_{0}^{A} \right\rangle \left| \Psi_{0}^{B} \right\rangle$$

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- GOOD CC theories can be systematically improved.
- GOOD CCSD(T) is a very accurate theory. Here single and double excitations are included as described above and triple excitations are included through a perturbative treatment.
- GOOD Size-extensive.
- BAD Computationally very expensive: CCSD(T) scales as $\mathcal{O}(N^7)$. So double the system size and the calculation costs 128 times more.
- BAD (kind of!) These are single-determinant theories as described. If the system is multi-configurational (more than one state contributing dominantly) the standard CC methods are not appropriate.

Basis sets	CI	СС	MBPT	Summary
CCSD: Exa	mples l			



Fig. 13.4. The weights of the Hartree–Fock determinant and of the six lowest excitation levels in the normalized CCSD (thin black lines) and FCI (thick grey lines) wave functions, plotted as functions of the number of noninteracting water monomers in the cc-pVDZ basis.

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

Brief recap of Raleigh-Schrödinger perturbation theory:

• Split the Hamiltonian into two parts:

 $\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{V}$

where \mathcal{H}_0 is a Hamiltonian which we know how to solve and \mathcal{V} contains that troublesome parts. We expect \mathcal{V} to be a perturbation so it must be small in some sense. λ is a complex number that will be 1 for the physical solution.

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Møller–Plesset Perturbation Theory II

• Let the solutions of \mathcal{H}_0 be:

$${\cal H}_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)}$$

Here the '0' indicates that these eigenvalues and eigenfunctions are of *zeroth*-order in the perturbation \mathcal{V} . We will use the short-form:

$$|\Psi_i^{(0)}
angle\equiv|i
angle$$

• Express the solutions of $\mathcal H$ in a power-series:

$$\Psi_{i} = \Psi_{i}^{(0)} + \lambda \Psi_{i}^{(1)} + \lambda^{2} \Psi_{i}^{(2)} + \dots = \sum_{n} \lambda^{n} \Psi_{i}^{(n)}$$
$$E_{i} = E_{i}^{(0)} + \lambda E_{i}^{(1)} + \lambda^{2} E_{i}^{(2)} + \dots = \sum_{n} \lambda^{n} E_{i}^{(n)}$$

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Møller–Plesset Perturbation Theory III

• Energies can be calculated by collecting terms at various orders:

$$\begin{split} E_i^{(0)} &= \langle \Psi_i^{(0)} | \mathcal{H}_0 | \Psi_i^{(0)} \rangle = \langle i | \mathcal{H}_0 | i \rangle \\ E_i^{(1)} &= \langle \Psi_i^{(0)} | \mathcal{V} | \Psi_i^{(0)} \rangle = \langle i | \mathcal{V} | i \rangle \\ E_i^{(2)} &= \langle \Psi_i^{(0)} | \mathcal{V} | \Psi_i^{(1)} \rangle \end{split}$$

etc. for higher order terms.

• The first-order correction to the wavefunction is given by

$$|\Psi_{i}^{(1)}
angle = \sum_{n \neq 0} \frac{|n
angle \langle n|\mathcal{V}|i
angle}{E_{i}^{(0)} - E_{n}^{(0)}}$$

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Møller–Plesset Perturbation Theory IV

• So we get

$$E_i^{(2)} = \sum_{n \neq 0} \frac{|\langle n | \mathcal{V} | i \rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

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Møller–Plesset Perturbation Theory V

Many-body perturbation theory (MBPT) starts from Hartree–Fock theory:

$$\mathcal{H}_{0} = \sum_{i=1}^{N} f(i) = \sum_{i=1}^{n} \left(h(i) + v^{\mathrm{HF}}(i) \right)$$
(10)

where $h(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}}$ We can now define the perturbation as

$$\mathcal{V} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} v^{\text{HF}}(i)$$
(11)

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Unlike $v^{\rm HF}$, the perturbation ${\cal V}$ is a 2-electron operator.

Møller–Plesset Perturbation Theory VI

MBPT energy at λ^0 :

$$E_0^{(0)} = \langle 0 | \mathcal{F} | 0
angle = \sum_{a \in ext{occ}} \epsilon_a$$

At first-order we get (no proof):

$$E_{0}^{(1)}=-rac{1}{2}\sum_{a=1,b=1}^{N}\left[\langle ab|r_{12}^{-1}|ab
angle -\langle aa|r_{12}^{-1}|bb
angle
ight]$$

We have not seen this before, but the sum of $E_0^{(0)}$ and $E_0^{(1)}$ is just the Hartree–Fock ground state energy:

$$E^{\rm HF} = E_0^{(0)} + E_0^{(1)} \tag{12}$$

This means that we need to get to at least second-order in perturbation theory to go beyond the Hartree–Fock description.

Møller–Plesset Perturbation Theory VII

Here is what the second-order MBPT energy expression looks like:

$$E_{0}^{(2)} = \sum_{a,b>a}^{\text{occ}} \sum_{r,s>r}^{\text{vir}} \frac{\left[\langle ab|r_{12}^{-1}|rs\rangle - \langle ab|r_{12}^{-1}|sr\rangle\right]^{2}}{\epsilon_{r} + \epsilon_{s} - \epsilon_{a} - \epsilon_{b}}$$
(13)

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This expression is termed as MBPT2 or MP2. The latter name comes from the other name for this kind of perturbation theory: Møller–Plesset perturbation theory.



- BAD A problem with Møller–Plesset perturbation theory: it diverges! See Olsen *et al.* J. Chem. Phys. **112**, 9736 (2000) for details. We now rarely go beyond MP2 in practical calculations.
- GOOD MP2 contains correlation.
- BAD But not enough correlation. Problems with systems with small HOMO-LUMO gaps (band gap — HOMO is highest occupied MO and LUMO is lowest unoccupied MO).
- GOOD (kind of!) It has a computational cost of O(N⁵). I.e., double the system in size and it will cost 32 times more computational power.

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• GOOD MBPT is size-consistent

Basis sets	CI	CC	MBPT	Summary
Which me	thod and ba	sis? I		

The Gold Standard:

CCSD(T) / aug-cc-pVTZ (or larger)

If not, use MP2, but with caution! Or else, use DFT (next lecture).

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