# Theoretical Overview

Alston J. Misquitta

Centre for Condensed Matter and Materials Physics
Queen Mary, University of London

January 22, 2020

# 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:

$$\chi(x) = \begin{cases} \psi(r)\alpha(\omega) \\ \psi(r)\beta(\omega) \end{cases} \tag{1}$$

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: A possible wavefunction is the Hartree product (HP):

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

However because $\Psi^{\mathrm{HP}}(x_1, x_2) \neq \Psi^{\mathrm{HP}}(x_2, x_1)$, the Hartree product is not allowed for idential particles.
We can symmetrize the wavefunction using:

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

but this function is not suitable for the electronic wavefunction.

# 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

$$\Psi(x_1, x_2, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \tag{2}$$

$$\equiv |\chi_i \chi_j \cdots \chi_k\rangle \tag{3}$$

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

# Many-electron basis VI

The exact $N$-electron wavefunction cannot, in general, be represented as a single Slater determinant: instead it is represented as a linear combination of determinants spanning a complete $N$-electron Hilbert space:

$$\Psi_{\mathrm{exact}} = \sum_i c_i \Psi_i, \tag{4}$$

where the coefficients $c_i$ may be complex.

I suspect that the above is not quite correct: Hilbert spaces are function spaces and these cannot be generally represented with a set of countable basis functions (in the above I have assumed this using a discrete sum). This is not too complicated: you know that only the bound eigenstates of the hydrogen atom are countable; the unbound states are uncountable — their energies form a continuous spectrum.

# Hartree–Fock equations I

We will now describe the ground state of our *N*-electron system with the BO approximation using a *single* Slater determinant:

$$\Psi_0(x_1, x_2, \cdots, x_N) = |\chi_1 \chi_2 \cdots \chi_N\rangle \tag{5}$$

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

$$E_0 \leq E^{\mathrm{HF}} = \min \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle \tag{6}$$

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

# Hartree–Fock equations II

We will later show using the variational principle that on minimization we get the following equations for the spin-orbitals:

$$f(i)\chi(x_i) = \epsilon\chi(x_i) \tag{7}$$

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

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + v^{\mathrm{HF}}(i) \tag{8}$$

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.

# Hartree–Fock equations III

These are called the 'self-consistent' set of equations as the Fock operator itself depends on the solutions.

The Fock equations cannot be solved directly (except for the Hydrogen atom), but since these are one-electron equations we solve them using a basis (details later):

- Introduce a basis for the spatial part of spin-orbitals:

  $$\chi_i(r) = \sum_m C_{im}\phi_m(r) \tag{9}$$

  The basis-functions $\{\phi_m\}$ are fixed functions that we need to choose. They determine the size of the vector space we operate in: the larger the better (mostly!).
- Using the linear variational principle, this leads to linear equations:

  $$\mathbf{FC} = \epsilon\mathbf{SC} \tag{10}$$

# Hartree–Fock equations IV

- And we solve these to obtain as many solutions as we had basis functions (times 2 if we allowed the spin up and spin down solutions to differ).
- The Hartree–Fock solution will normally be the one in which we have electrons occupying the lowest energy spin-orbitals.

Q: How do we choose the basis?

# Slater-type orbitals I

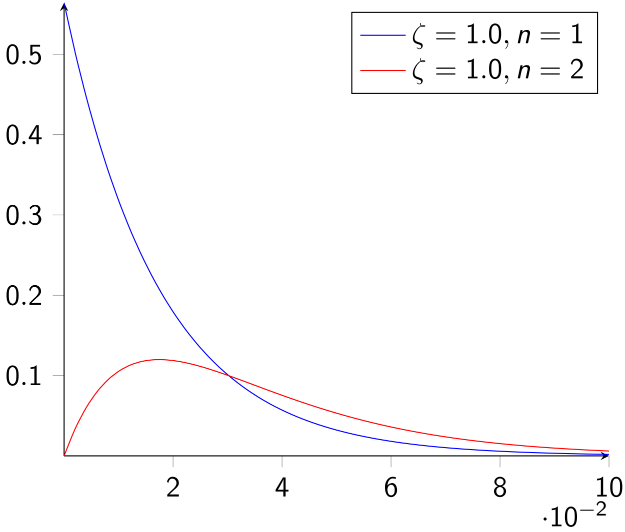
A reasonable choice for basis sets for finite systems would be what are called Slater-type orbitals: these are very like solutions of the 1-electron Hamiltonian. They differ in two ways: (1) the radial part is simpler and (2) the exponent is not integral but can be varied to account for *screening* effects.

$$\phi = R_{nl}(r)\mathcal{Y}_{lm}(\theta,\phi) \tag{11}$$

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

$$R_{nl}(r) = \frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} \tag{12}$$

# Slater-type orbitals II



# Slater-type orbitals III

Comments on Slater-type orbitals:

- GOOD Nuclear cusp condition satisfied.

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

- 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

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

  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):

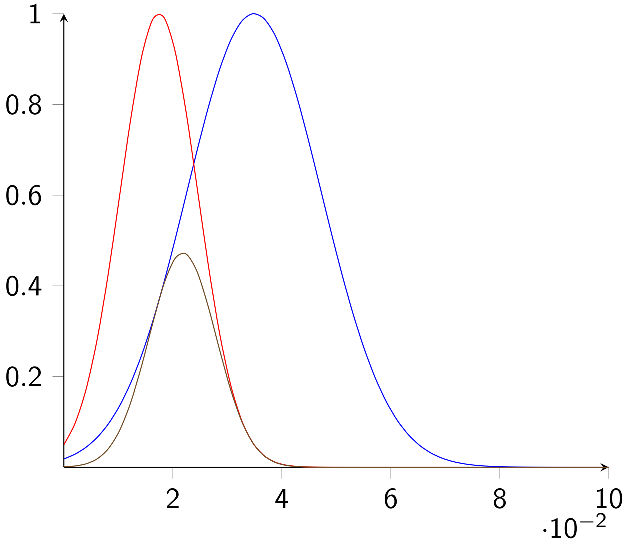
$$R_{nl} \sim r^n e^{-\alpha(r-\mathbf{A})^2} \tag{13}$$

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

- 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.

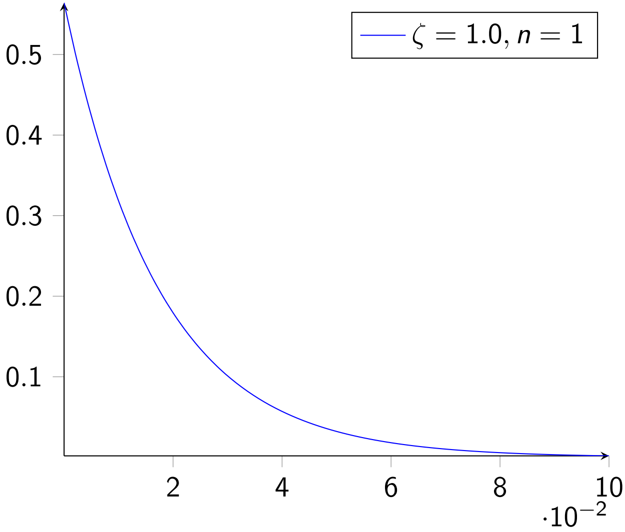
The two negative points can, to some extent, be remedied by using not single GTOs, but *linear combinations* of GTOs. These groups of GTOs are termed *contractions*.
Basis sets consist of groups of contractions together with some un-contracted GTOs. The better the basis, the more of these there will be and the more GTOs in a contraction.

# Gaussian-type orbitals (GTOs) IV

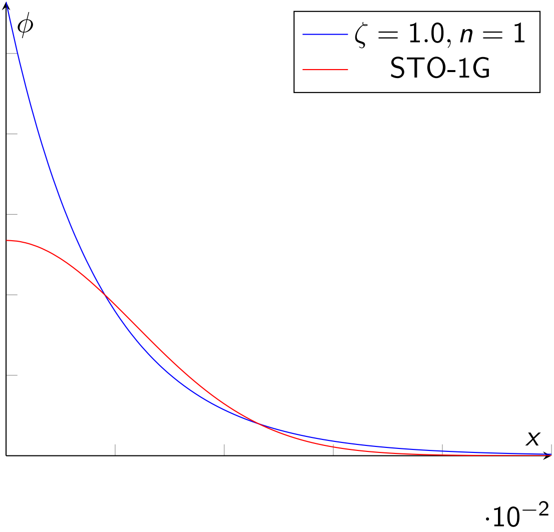
cc-pvDZ Dunning basis for hydrogen:

```
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
```

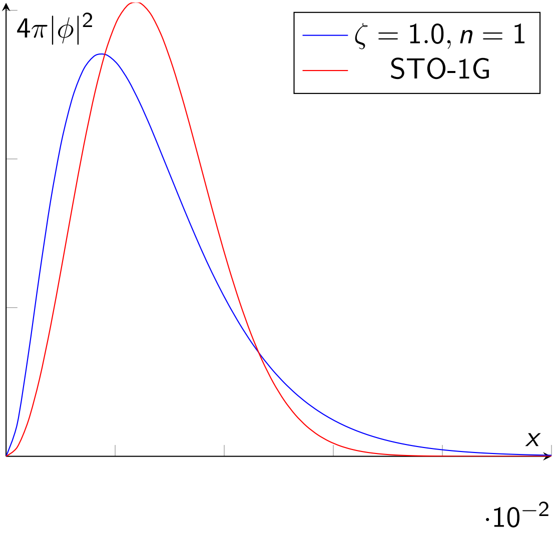
# Gaussian-type orbitals (GTOs) V



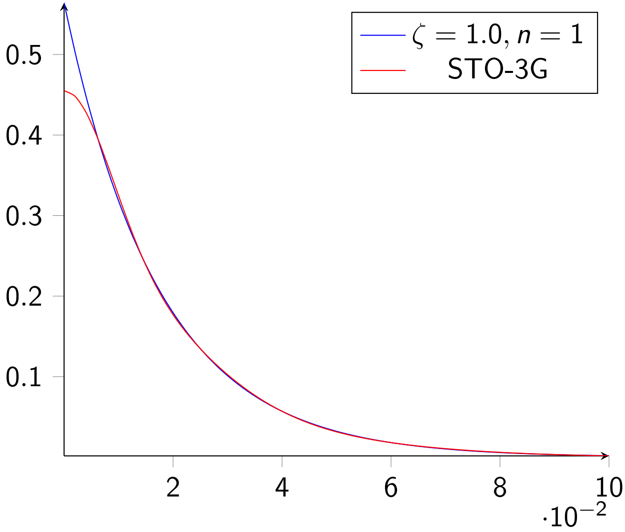
# Gaussian-type orbitals (GTOs) VI



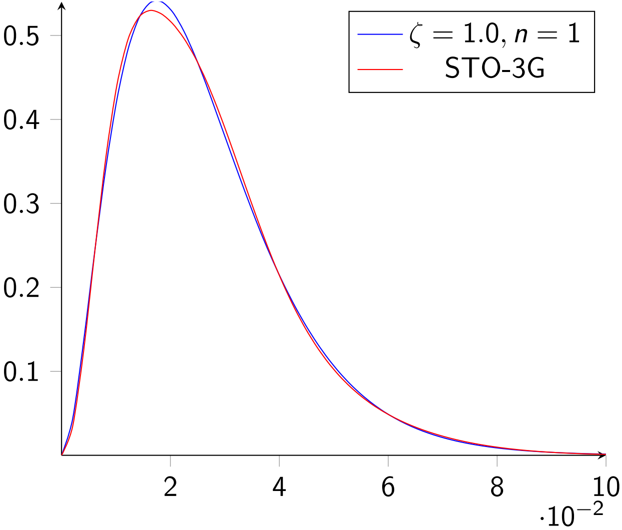
# Gaussian-type orbitals (GTOs) VII



# Gaussian-type orbitals (GTOs) VIII



# Gaussian-type orbitals (GTOs) IX



# Gaussian-type orbitals (GTOs) X

Basis set recommendations:

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

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

# Correlation I

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

We know that the Hartree–Fock ground state energy $E_0$ will be an *upper bound* to the exact ground-state energy $\mathcal{E}_0$. The difference

$$E_{\rm corr} = \mathcal{E}_0 - E_0$$

is called the *correlation energy*. This energy is often large enough that we cannot neglect it. The question now is how do we calculate $E_{\rm corr}$?

# Correlation II

To calculate $E_{\mathrm{corr}}$ we need to use what are known as post-Hartree–Fock methods. Amongst the main-stream approaches are

- **Configuration Interaction (CI)**: Create a linear expansion of determinants created from the HF ground-state determinant by exciting electrons into the virtual space.
- **Perturbation Theory (MP*n*)**: Develop a perturbative expansion starting with the Hartree–Fock ground state as the zeroth order solution.
- **Coupled-cluster methods (CC)**: Like CI, but with infinite-order summations.
- **Quantum Montecarlo (QMC)**: Variational Montecarlo (VMC), Diffusion Montecarlo (DMC), full configuration interaction quantum montecarlo (FCIQMC).

# Correlation III

- **Density-functional theory (DFT)**: Reformulate the problem in terms of the electron density.
- **Density matrix theory**: Variant of the above that recognises that uses the two-electron density.
- **Greens function methods**.....

Here we will look at CI, CC, MP2 and (finally) DFT. The other methods require another course altogether!

# Configuration Interaction I

How do we improve on HF?
We know that the exact $N$-electron wavefunction is represented as a linear combination of determinants spanning a complete $N$-electron Hilbert space:

$$\Psi_{\mathrm{exact}} = \sum_i c_i \Psi_i. \tag{14}$$

CI: Define these extra determinants from *excitations* of the HF wavefunction:

$$|\Psi\rangle = c_0|\Psi_0\rangle + \sum_{ia} c_i^a |\Psi_i^a\rangle + \sum_{i<j,a<b} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \cdots$$

Q: What are excited states and how to we form them?

# Configuration Interaction II

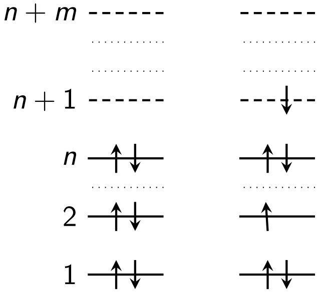


Figure: Left: HF ground state configuration. Right: An example of an excited state configuration. If there are $n$ occupied levels (2 electrons each, so $N = 2n$) and $m$ virtual (un-occupied) levels, in how many ways can we form excited states? Each of these states will correspond to a Slater determinant.

# Configuration Interaction III

The Full CI (FCI) wavefunction:

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

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

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

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

# 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.

$$
\begin{aligned}
|\Psi^{\mathrm{CID}}\rangle &= |\Psi_0\rangle + \sum_{ij,ab} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle \\
&= |\Psi_0\rangle + c_D |D\rangle
\end{aligned}
$$

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 $E(N) = N \times E(1)$.

# 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:

$$|\Psi^{\mathrm{CC}}\rangle = \exp(\hat{T})|\Psi_0\rangle$$

where $\hat{T}$ is an appropriate excitation operator.

# Coupled-cluster Theory II

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

$$\begin{aligned}|\Psi^{\mathrm{CCD}}\rangle &= \exp(\hat{T}_2)|\Psi_0\rangle \\ &= (1 + \hat{T}_2 + \frac{1}{2!}\hat{T}_2\hat{T}_2 + \cdots)|\Psi_0\rangle\end{aligned}$$

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

# Coupled-cluster Theory III

- 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.

# Møller–Plesset Perturbation Theory I

- Based on 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.

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

$$\mathcal{H}_0 = \sum_{i=1}^{N} f(i) = \sum_{i=1}^{n} \left(h(i) + v^{\mathrm{HF}}(i)\right) \qquad (15)$$

where $h(i) = -\frac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}}$

# Møller–Plesset Perturbation Theory II

- We can now define the perturbation as

$$\mathcal{V} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} v^{\mathrm{HF}}(i) \tag{16}$$

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

- The zeroth and first-order MBPT terms are included in the Hartree-Fock energy, so the first term beyond this one is the second-order expression:

$$E_0^{(2)} = \sum_{a,b>a}^{\mathrm{occ}} \sum_{r,s>r}^{\mathrm{vir}} \frac{\left[\langle ab|r_{12}^{-1}|rs\rangle - \langle ab|r_{12}^{-1}|sr\rangle\right]^2}{\epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b} \tag{17}$$

  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.

# Møller–Plesset Perturbation Theory III

- 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 $\mathcal{O}(N^5)$. I.e., double the system in size and it will cost 32 times more computational power.
- GOOD MBPT is *size-consistent*

# Which method and basis? I

Practical considerations: CI, CC and MP2 are expensive!

| Method | Cost | Description |
|---|---|---|
| HF | $N^4$ | Starting point for correlated methods. |
| MP2 | $N^5$ | OK. Useful for optimizations. |
| CISD | $N^6$ | Not size-consistent. |
| CCSD(T) | $N^7$ | Very accurate. |
| DFT | $N^3$ | Accurate, but with systematic shortcomings. |

All correlated methods require large basis sets with high angular functions.

# Apparent and intrinsic errors I

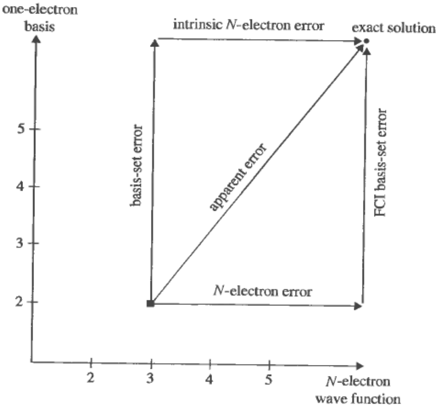


**Fig. 15.1.** The errors in quantum-chemical calculations.

# Apparent and intrinsic errors II

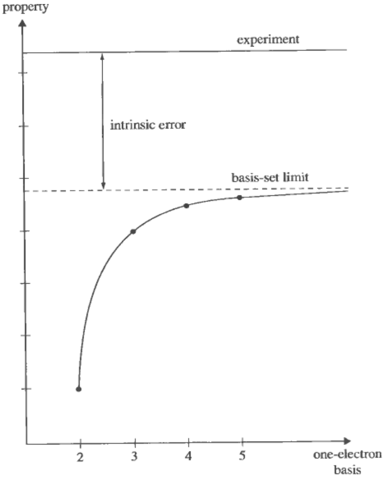


**Fig. 15.2.** The dependence of the calculated property on the quality of the basis.

# Apparent and intrinsic errors III

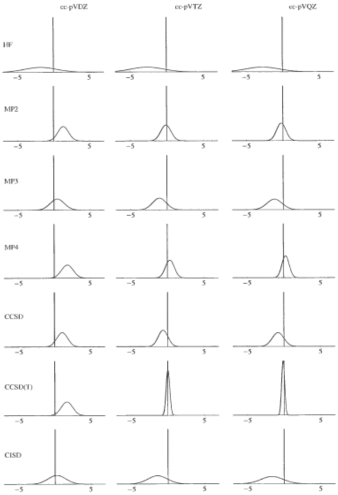


**Fig. 15.4.** Normal distributions of the errors in the calculated bond distances (pm). For ease of comparison, all distributions have been normalized to one and plotted against the same horizontal and vertical scales.

# Apparent and intrinsic errors IV

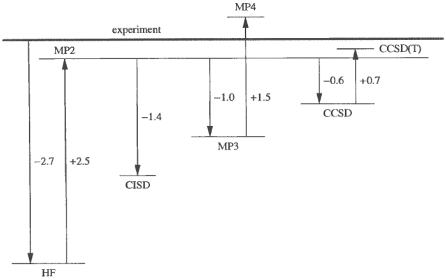


**Fig. 15.5.** The relationships between the calculated equilibrium bond distances for the standard models (in pm).

# Summary 1 I

**Which Method should I use?**

The Gold Standard:

CCSD(T) / aug-cc-pVTZ (or larger)
BAD: Cannot be used on periodic systems. . . yet!

If not, use MP2, but with caution! Or else, use DFT!

# Density-Functional Theory I

Hohenberg & Kohn (Phys. Rev. B, **136**, 864 (1964)):

**Theorem**

*H–K Theorem 1 There is a one-to-one mapping between the electronic density and the external potential, and hence, the Hamiltonian:*

$$\rho(\mathrm{r}) \Longleftrightarrow \mathcal{H}$$

Proof is by *reductio ad absurdum*. We will prove it later, but try it yourself.

# Density-Functional Theory II

E. Bright Wilson's observation: To know the Hamiltonian we need to know the number of electrons and position and charge of the nuclei. These can be obtained from the density:

- $N = \int \rho(\mathrm{r}) \mathrm{dr}$
- Position and charge of nuclei can be obtained from the cusps:

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

So $\rho$ completely determines the Hamiltonian and therefore the ground-state energy (and also all excited state energies!).

# Density-Functional Theory III

What the Hohenberg–Kohn theorem allows us to do is (formally) write the energy as a *functional* of the density.

$$\begin{aligned} E = E[\rho] &= T[\rho] + V_{\mathrm{ee}}[\rho] + V_{\mathrm{en}}[\rho] \\ &= F[\rho] + \int \rho(\mathrm{r})\mathrm{v}_{\mathrm{ext}}(\mathrm{r})\mathrm{dr} \end{aligned}$$

We will later show that this can be written as

$$E[\rho] = T_{\mathrm{S}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] + \int v_{\mathrm{ext}}(\mathrm{r})\rho(\mathrm{r})\mathrm{dr} \qquad (18)$$

where $T_{\mathrm{S}}[\rho]$ is the kinetic energy functional, $J[\rho]$ is the Classical Coulomb energy functional — these two are known — and all the unknown stuff is swept into the so-called *exchange-correlation functional*, $E_{\mathrm{xc}}[\rho]$.

# Density-Functional Theory IV

What is the exchange-correlation (XC) energy functional?

If we knew $E_{\mathrm{xc}}[\rho]$ and could compute it effeciently, that would be all we'd talk about in a course like this. But we don't know it exactly; all we have are approximations, and each approximation has weaknesses.

Common approximations are

- LDA : Local density approximation
- PBE : Perdew–Burke–Wang functional
- BLYP : From A. Becke with the LYP correlation functional.
- B3LYP, PBE0, B97....

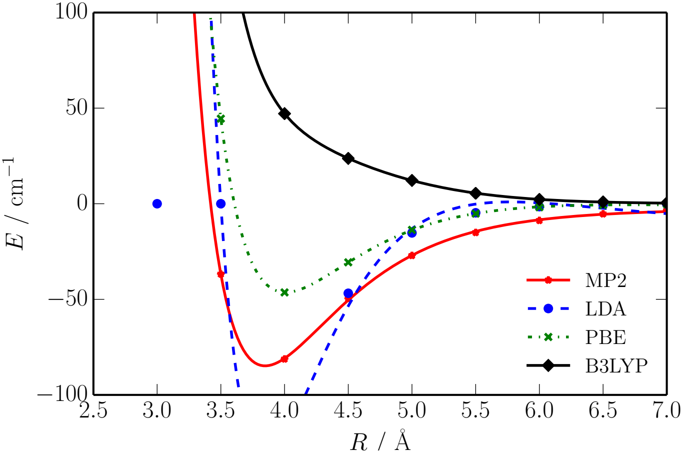
# Density-Functional Theory V

- In a sense, what Kohn & Sham did was to sweep all the unknowns under the rug. But they did this intelligently as they had a good idea of how to approximate the unknown bits: the exchange-correlation energy and its functional derivative.
- Also, they knew that their formalism was *in principle* exact as they had proved various theorems to that effect.
- It turned out that their proofs were not mathematically sound, but this was fixed by others.
- The rest of the DFT story is how we find the exchange-correlation functional $E_{\rm xc}[\rho]$.

# DFT has systematic problems I

Our approximate DFT models all have problems. Two of the biggest are the *self-iteraction error* and the *lack of the dispersion energy*. Let's look at the latter.
Consider the argon dimer: this is a dispersion-bound system, that is, the attraction between two argon atoms arises purely from the dispersion interaction. This is typical of the rare-gas atoms. On the next slide we see interaction energies calculated for this system with MP2, LDA, PBE and B3LYP using the `aug-cc-pVTZ` basis set using the counterpoise correction.

# DFT has systematic problems II



# DFT has systematic problems III

There are ways of reducing both problems and we will focus a good deal on these. It is very important that you understand the weaknesses of the methods you use, as this then leads to ways in which these weaknesses may be fixed.

# Which method? I

Practical considerations: CI, CC and MP2 are expensive!

| Method | Cost | Description |
|---|---|---|
| HF | $N^4$ | Starting point for correlated methods. |
| MP2 | $N^5$ | OK. Useful for optimizations. |
| CISD | $N^6$ | Not size-consistent. |
| CCSD(T) | $N^7$ | Very accurate. |
| DFT | $N^3$ | Accurate, but with systematic shortcomings. |

All correlated methods require large basis sets with high angular functions.

# Which method? II

The Gold Standard:

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

If not, use MP2, but with caution! Or else, use DFT — also with caution!

# There's more I

Electronic structure theory does not end with these methods; there is much more:

- Intermolecular perturbation theory. (this is my own work)
- Stochastic methods. QMC, DMC, FCIQMC — the last one is very neat and has revolutionised the field.
- Non-adiabatic method in which the Born–Oppenheimer approximation is not used.
- Methods that treat the nuclei quantum mechanically.
- Methods that use the Dirac equation to include relativistic effects and effects from QED.
- Quantum algorithms for Quantum Computers??? Pure speculation of course, but who knows!