Electronic Structure Theory

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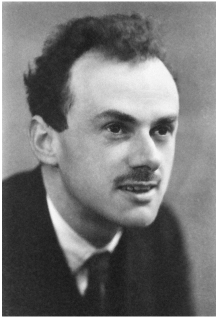
> “The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.”
>
> – Paul Dirac



The Quantum Theory of Molecules

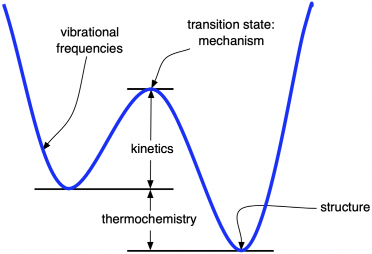
According to quantum mechanics, the state of a molecule is governed by the time-depedent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

The Born–Oppenheimer approximation adiabatically separates the electronic and nuclear degrees of freedom

$$\hat{H}_e\Psi_e(\mathbf{x}) = E_e\Psi_e(\mathbf{x})$$
$$i\hbar\frac{\partial}{\partial t}\Psi_n(\mathbf{X},t) = (\hat{H}_n + E_e)\Psi_n(\mathbf{X},t)$$

The nuclei experience an effective potential energy surface $V_n(\mathbf{X}) + E_e(\mathbf{X})$



This course concerns how to solve $\hat{H}_e\Psi_e(\mathbf{x}) = E_e\Psi_e(\mathbf{x})$

Course Outline

- Hartree–Fock theory: the independent electron model
  - The Hartree–Fock wavefunction
  - The Hartree–Fock equations
  - Interpreting the solutions
- Electron correlation: configuation interaction theory
- Electron correlation: density functional theory

Further reading

- Atkins & Freedman, *Molecular Quantum Mechanics (5th Ed) Ch 8 and 9*
- Frank Jensen, *Introduction to Computational Chemistry* (Wiley, 2007)
- Szabo and Ostlund, *Modern Quantum Chemistry* (Dover, 1996)
- Tew *et al* J Comput Chem 28: 1307, 2007, *Electron correlation: The many-body problem at the heart of chemistry*

Molecular Orbital Theory

In the independent electron model, each electron is thought to occupy a molecular orbital with either up or down spin. According to the Pauli exclusion principle, each electron must occupy a different spin orbital.

The corresponding n-electron wavefunction is the Hartree product

$$\psi(\mathbf{x}_1, \dots \mathbf{x}_n) = \prod_i^n \phi_i(\mathbf{x}_i)$$

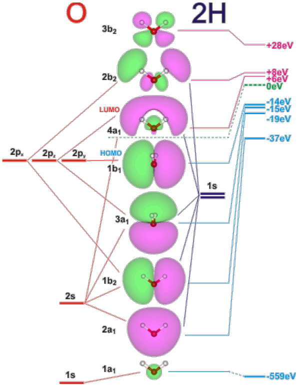
Notation: $\phi_i(\mathbf{x}) = \varphi_i(\mathbf{r})\sigma(s)$

$\phi_i(\mathbf{x})$ spin-orbital

$\varphi_i(\mathbf{r})$ orbital

$\sigma(s)$ spin function (α or β)

Orthonormality is assumed: $\langle\phi_i|\phi_j\rangle = \delta_{ij}$, $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$, $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$, $\langle\alpha|\beta\rangle = 0$



e.g. $\phi_5(\mathbf{x}) = \varphi_{1b_1}(\mathbf{r})\alpha(s)$

Fermi antisymmetry

The Pauli exclusion principle is a consequence of Fermi antisymmetry.

Since electrons are indistinguishable, physical properties are invariant with repect to electron swaps. Consider the probability distribution function

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1, \ldots \mathbf{x}_n)|^2$$

$$\Rightarrow \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n) = \pm\Psi(\mathbf{x}_2, \mathbf{x}_1, \ldots \mathbf{x}_n) \qquad \begin{cases} + & \text{bosons} \\ - & \text{fermions} \end{cases}$$

Fermionic antisymmetry is imposed by applying the antisymmetric operator

$$\hat{A} = \frac{1}{n!}\sum_{\mu}(-1)^{p_\mu}\hat{\pi}_\mu$$

permutation $\hat{\pi}_\mu$
parity p_μ

$\hat{A}$ is a projection operator onto the completely antisymmetric state.
$\hat{A}$ is hermitian $\hat{A}^\dagger = \hat{A}$. All projection operators are idempotent: $\hat{A}\hat{A} = \hat{A}$

The Slater determinant

The Hartree–Fock wavefunction is the antisymmetrised Hartree product.

$$\begin{aligned}\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) &= \sqrt{n!}\,\hat{A}\,\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\cdots\phi_n(\mathbf{x}_n) \\ |\psi\rangle &= \sqrt{n!}\,\hat{A}\,|\phi_1\phi_2\cdots\phi_n\rangle \qquad \text{(Dirac notation)} \\ \langle\psi| &= \sqrt{n!}\,\langle\phi_1\phi_2\cdots\phi_n|\,\hat{A}\end{aligned}$$

The Hartree–Fock wavefunction is also referred to as a Slater determinant

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \cdots & \phi_n(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \cdots & \phi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_n) & \phi_2(\mathbf{x}_n) & \cdots & \phi_n(\mathbf{x}_n) \end{vmatrix}$$

Can mix the occupied orbitals arbitrarily without changing the wavefunction $|U\Phi| = |U||\Phi| = e^{i\theta}|\Phi|$

Normalisation

The wavefunction is normalised if the overlap $\langle\psi|\psi\rangle = 1$.

$$\begin{aligned}
\langle\psi|\psi\rangle =& n!\langle\phi_1(\mathbf{x}_1)\cdots\phi_n(\mathbf{x}_n)|\,\hat{A}\,\hat{A}\,|\phi_1(\mathbf{x}_1)\cdots\phi_n(\mathbf{x}_n)\rangle \\
=& n!\langle\phi_1(\mathbf{x}_1)\cdots\phi_n(\mathbf{x}_n)|\,\hat{A}\,|\phi_1(\mathbf{x}_1)\cdots\phi_n(\mathbf{x}_n)\rangle \\
=& \sum_\mu (-1)^{p_\mu}\langle\phi_1(\mathbf{x}_1)\cdots\phi_n(\mathbf{x}_n)|\hat{\pi}_\mu\,|\phi_1(\mathbf{x}_1)\cdots\phi_n(\mathbf{x}_n)\rangle \\
=& +\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle\langle\phi_3|\phi_3\rangle\cdots\langle\phi_n|\phi_n\rangle \\
& -\langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle\langle\phi_3|\phi_3\rangle\cdots\langle\phi_n|\phi_n\rangle \\
& +\ldots \qquad\qquad \text{n! terms} \\
=& \langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle\langle\phi_3|\phi_3\rangle\cdots\langle\phi_n|\phi_n\rangle \qquad \text{only one survives} \\
=& 1
\end{aligned}$$

We have factorised the many-electron integral and used orthonormality $\langle\phi_i|\phi_j\rangle = \delta_{ij}$

$$\int\!\!\int\phi_i^*(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_j(\mathbf{x}_1)\phi_l(\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2 = \int\phi_i^*(\mathbf{x}_1)\phi_j(\mathbf{x}_1)d\mathbf{x}_1\int\phi_k^*(\mathbf{x}_2)\phi_l(\mathbf{x}_2)d\mathbf{x}_2 = \delta_{ij}\delta_{kl}$$

The electron density

The electron density at $\mathbf{r}$ is the sum of the probabilities of finding each electron at that point in space

$$\begin{aligned}\rho(\mathbf{r}) =& \langle\Psi|\sum_{i=1}^{n}\delta(\mathbf{r}-\mathbf{r}_i)|\Psi\rangle \\ =& n\int \Psi^*(\mathbf{x},\mathbf{x}_2\ldots\mathbf{x}_n)\Psi(\mathbf{x},\mathbf{x}_2\ldots\mathbf{x}_n)\, ds d\mathbf{x}_2\ldots d\mathbf{x}_n\end{aligned}$$

For a Slater determinant wavefunction, this reduces to the sum of probabilities for each occupied orbital

$$\rho(\mathbf{r}) = \sum_{i=1}^{n}|\varphi_i(\mathbf{r})|^2$$

The integral of $\rho(\mathbf{r})$ is always equal to the number of electrons

$$n = \int \rho(\mathbf{r})\, d\mathbf{r}$$

The Hartree–Fock Energy

The independent particle model is an approximation when $n > 1$. The best wavefunction of this from is the one with the lowest energy.

The energy is given by the expectation value

$$\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle = \langle \psi | \sum_{i}^{n} \hat{h}_i + \sum_{i<j}^{n} \hat{g}_{ij} | \psi \rangle$$

Reminder [atomic units $\hbar = 4\pi\epsilon_0 = m_e = e = 1$]

$$\hat{h}_i = \hat{T}_i + \hat{v}(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 - \sum_{I} \frac{Z_I}{r_{iI}} \qquad \text{one-electron}$$

$$\hat{g}_{ij} = \frac{1}{r_{ij}} \qquad \text{two-electron}$$

Let us consider the one-electron and two-electron energies separately

one-electron terms

Since $\hat{h} = \sum_i^n \hat{h}_i$ is completely symmetric, $[\hat{A}, \hat{h}] = 0$

$$\begin{aligned}
\langle\psi| \sum_i^n \hat{h}_i |\psi\rangle &= n! \langle\phi_1 \dots \phi_n| \hat{A} \sum_i^n \hat{h}_i \hat{A} |\phi_1 \dots \phi_n\rangle \\
&= n! \langle\phi_1 \dots \phi_n| \sum_i^n \hat{h}_i \hat{A} |\phi_1 \dots \phi_n\rangle \\
&= \langle\phi_1 \dots \phi_n| \sum_i^n \hat{h}_i \sum_\mu (-1)^{p_\mu} \hat{\pi}_\mu |\phi_1 \dots \phi_n\rangle
\end{aligned}$$

Recall that $\hat{A} = \frac{1}{n!} \sum_\mu (-1)^{p_\mu} \hat{\pi}_\mu$ and $\hat{A}\hat{A} = \hat{A}$

Let us consider the terms $\hat{h}_1$ and $\hat{h}_2$ etc one by one

one-electron terms

$$\langle\psi|\sum_i^n \hat{h}_i|\psi\rangle = \langle\phi_1\dots\phi_n|\sum_i^n \hat{h}_i \sum_\mu (-1)^{p_\mu}\hat{\pi}_\mu|\phi_1\dots\phi_n\rangle$$

The contribution from $\hat{h}_1$ is

$$\begin{aligned}\langle\phi_1\dots\phi_n|\hat{h}_1\sum_\mu(-1)^{p_\mu}\hat{\pi}_\mu|\phi_1\dots\phi_n\rangle &= +\langle\phi_1|\hat{h}_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle\cdots\langle\phi_n|\phi_n\rangle\\ &\quad -\langle\phi_1|\hat{h}_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle\cdots\langle\phi_n|\phi_n\rangle\\ &\quad +\dots \qquad \text{n! terms}\\ &= \langle\phi_1|\hat{h}_1|\phi_1\rangle\end{aligned}$$

Similarly, for $\hat{h}_2$

$$\begin{aligned}\langle\phi_1\dots\phi_n|\hat{h}_2\sum_\mu(-1)^{p_\mu}\hat{\pi}_\mu|\phi_1\dots\phi_n\rangle &= \langle\phi_1|\phi_1\rangle\langle\phi_2|\hat{h}_2|\phi_2\rangle\cdots\langle\phi_n|\phi_n\rangle\\ &= \langle\phi_2|\hat{h}_2|\phi_2\rangle\end{aligned}$$

So we find

$$\langle\psi|\sum_i^n \hat{h}_i|\psi\rangle = \sum_{i=1}^n\langle\phi_i|\hat{h}_i|\phi_i\rangle$$

two-electron terms

Since $\hat{g} = \sum_{i<j}^{n} \hat{g}_{ij}$ is also completely symmetric, $[\hat{A}, \hat{g}] = 0$

$$\begin{aligned}
\langle\psi|\sum_{i<j}^{n}\hat{g}_{ij}|\psi\rangle &= n!\langle\phi_1\ldots\phi_n|\hat{A}\sum_{i<j}^{n}\hat{g}_{ij}\hat{A}|\phi_1\ldots\phi_n\rangle \\
&= n!\langle\phi_1\ldots\phi_n|\sum_{i<j}^{n}\hat{g}_{ij}\hat{A}|\phi_1\ldots\phi_n\rangle \\
&= \langle\phi_1\ldots\phi_n|\sum_{i<j}^{n}\hat{g}_{ij}\sum_{\mu}(-1)^{p_\mu}\hat{\pi}_\mu|\phi_1\ldots\phi_n\rangle
\end{aligned}$$

Let us consider the first term $\hat{g}_{12}$

two-electron terms

$$
\begin{aligned}
\langle\phi_1\dots\phi_n|\hat{g}_{12}\sum_\mu(-1)^{p_\mu}\hat{\pi}_\mu|\phi_1\dots\phi_n\rangle \\
&= +\langle\phi_1\phi_2|g_{12}(1-\pi_{12})|\phi_1\phi_2\rangle\langle\phi_3|\phi_3\rangle\cdots\langle\phi_n|\phi_n\rangle \\
&\quad -\langle\phi_1\phi_2|g_{12}(1-\pi_{12})|\phi_3\phi_2\rangle\langle\phi_3|\phi_1\rangle\cdots\langle\phi_n|\phi_n\rangle \\
&\quad +\dots \qquad \text{n!/2 terms} \\
&= \langle\phi_1\phi_2|g_{12}(1-\pi_{12})|\phi_1\phi_2\rangle
\end{aligned}
$$

Therefore the total two-electron energy is

$$
\begin{aligned}
\langle\psi|\sum_{i<j}^n\hat{g}_{ij}|\psi\rangle &= \sum_{i<j}^n\langle\phi_i\phi_j|\hat{g}_{ij}(1-\pi_{ij})|\phi_i\phi_j\rangle \\
&= \frac{1}{2}\sum_{ij}^n\langle\phi_i\phi_j|\hat{g}_{ij}(1-\pi_{ij})|\phi_i\phi_j\rangle \quad * \quad \text{more convenient}
\end{aligned}
$$

Although $(*)$ appears to erronesously include the repulsion of the electron in orbital i with itself, this is eliminated since $1-\pi_{ii}=0$.

The Hartree–Fock energy

The energy expectation value for the Hartree–Fock wavefunction is

$$\begin{aligned}\langle\psi|\hat{H}|\psi\rangle &= \sum_{i}^{n}\langle\phi_i|h_1|\phi_i\rangle + \frac{1}{2}\sum_{ij}^{n}\langle\phi_i\phi_j|(1-\hat{\pi}_{12})\hat{g}_{12}|\phi_i\phi_j\rangle \\ &= T + V + J - K\end{aligned}$$

The one-electron energy is $T + V$ where T is kinetic energy and V the potential energy of attraction of the electrons to the nuclei.

$$\begin{aligned}T + V &= \sum_{i}^{n}\langle\phi_i| - \frac{1}{2}\nabla^2|\phi_i\rangle + \sum_{i}^{n}\langle\phi_i|v(\mathbf{r})|\phi_i\rangle \\ &= \sum_{i}^{n}\langle\phi_i| - \frac{1}{2}\nabla^2|\phi_i\rangle + \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r}\end{aligned}$$

The Hartree–Fock energy

The energy expectation value for the Hartree–Fock wavefunction is

$$\begin{aligned}\langle\psi|\hat{H}|\psi\rangle &= \sum_{i}^{n}\langle\phi_i|h_1|\phi_i\rangle + \frac{1}{2}\sum_{ij}^{n}\langle\phi_i\phi_j|(1-\hat{\pi}_{12})\hat{g}_{12}|\phi_i\phi_j\rangle \\ &= T + V + J - K\end{aligned}$$

The two electron energy is $J - K$. The Coulomb energy J is the repulsion of the electron cloud with itself. K is the exchange stabilisation that

- eleminినates the repulsion of an electron with itself
- accounts for non-classical exchange stabilisation from the Fermi holes

$$\begin{aligned}J - K =& \frac{1}{2}\sum_{ij}^{n}\langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle - \frac{1}{2}\sum_{ij}^{n}\langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_j\phi_i\rangle \\ =& \frac{1}{2}\int\!\!\int\rho(\mathbf{r}_1)\frac{1}{r_{12}}\rho(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{2}\sum_{ij}^{n}\langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_j\phi_i\rangle\end{aligned}$$

Recap

- Hartree–Fock theory treats electrons as independent particles.
- The Hartree–Fock wavefunction is the antisymmetrised Hartree orbital product, where the orbitals are those that minimise the energy.

$$|\psi\rangle = \sqrt{n!}\,\hat{A}\,|\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\cdots\phi_n(\mathbf{x}_n)\rangle \qquad \text{Slater determinant}$$

- Gives the best molecular orbital depiction of the electronic structure.
- The Hartree-Fock energy $\langle\psi|\hat{H}|\psi\rangle = T + V + J - K$

$$T + V = \sum_i^n \langle\phi_i| - \frac{1}{2}\nabla^2 + v(\mathbf{r})|\phi_i\rangle \qquad \text{one-electron energy}$$

$$J = \frac{1}{2}\sum_{ij}^n \langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle \qquad \text{Coulomb energy}$$

$$K = \frac{1}{2}\sum_{ij}^n \langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_j\phi_i\rangle \qquad \text{exchange energy}$$

Wavefunction optimisation

- The independent particle model is an approximation when $n > 1$
- The variational principle alows us to optimise the wavefunction by varying the orbitals to minimise the energy

$$E[\phi] = \langle\psi(\phi)|\hat{H}|\psi(\phi)\rangle \geq E_{\text{exact}}$$

- The energy expression is only valid for orthonormal orbitals
  - Need Lagrange multipliers for constrained optimisation
- The wavefunction is a function of the orbitals
- The energy is a functional of the orbitals
  - Need calculus of variations

$$\frac{\delta E[\phi]}{\delta\phi_i} = 0$$

The Lagrangian

Optimisation of the energy subject to the constraint that the orbitals are orthonormal is acheived through the technique of Lagrange multipliers

$$L[\phi] = E[\phi] - \sum_{ij} \epsilon_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$

Stationarity of the Lagrangian with respect to the multipliers imposes the orthonormality constraint

$$\frac{\partial L}{\partial \epsilon_{ij}} = \langle \phi_i | \phi_j \rangle - \delta_{ij} = 0$$

Stationarity of the Lagrangian with respect to the orbitals minimises the energy subject to the constraint

$$\frac{\delta L}{\delta \phi_k} = 0$$

Functionals

A function maps a number to a number

$$\text{e.g.} \qquad f(x) = e^{-x}$$

- maps the number x to the number $f(x)$ using the expression e^{-x}

A functional maps a function to a number

$$\text{e.g.} \qquad F[f] = \int_V f^2(x)dx$$

- maps the function $f(x)$ to the number $F[f]$ using $\int_V f^2(x)dx$

In general, the integrand of the functional can be an arbitary expression of the function f, and its derivatives $\nabla f, \nabla^2 f, \ldots$

- $F[f] = \displaystyle\int_V F[\mathbf{x}, f, \nabla f, \nabla^2 f, \ldots]\, d\mathbf{x}$

Functional derivatives

The functional derivative $\frac{\delta F}{\delta f}(\mathbf{x})$ is the change in the number F due to a change in the function f at $\mathbf{x}$

$$\int_V \frac{\delta F}{\delta f}(\mathbf{x}) g(\mathbf{x})\, d\mathbf{x} = \frac{d}{d\epsilon} F(f + \epsilon g)\Big|_{\epsilon=0}$$

The formula for the functional derivative is

$$\frac{\delta F}{\delta f} = \frac{\partial F}{\partial f} - \nabla \cdot \frac{\partial F}{\partial \nabla f} + \nabla^2 \frac{\partial F}{\partial \nabla^2 f} - \dots$$

For a functional $F[f]$ where f is itself a functional of another function $g(\mathbf{x})$, we have the chain rule

$$\frac{\delta F}{\delta g(\mathbf{x})} = \int_V \frac{\delta F}{\delta f(\mathbf{x}')} \frac{\delta f(\mathbf{x}')}{\delta g(\mathbf{x})}\, d\mathbf{x}'$$

A functional $F[f]$ is stationary with respect to f if $\frac{\delta F}{\delta f}(\mathbf{x}) = 0$

The energy functional

The expected energy is a functional of the *n* occupied orbitals

$$E[\phi] = T[\phi] + V[\phi] + J[\phi] - K[\phi]$$

$$T[\phi] = \sum_{i}^{n} \int -\frac{1}{2}\phi_i^*(\mathbf{x}_1)\nabla^2\phi_i(\mathbf{x}_1)\, d\mathbf{x}_1$$

$$V[\phi] = \sum_{i}^{n} \int v(\mathbf{r}_1)\phi_i^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\, d\mathbf{x}_1$$

$$J[\phi] = \frac{1}{2}\sum_{ij}^{n} \iint \phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2$$

$$K[\phi] = \frac{1}{2}\sum_{ij}^{n} \iint \phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\phi_j(\mathbf{x}_1)\phi_i(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2$$

The Hartree–Fock orbitals are those where $\frac{\delta E}{\delta \phi_k} = 0$ for all k

The functional derivative of the potential energy

We need the functional derivative of the energy with repect to a change in one of the orbitals ϕ_k

$$\frac{\delta E}{\delta \phi_k} = \frac{\delta T}{\delta \phi_k} + \frac{\delta V}{\delta \phi_k} + \frac{\delta J}{\delta \phi_k} - \frac{\delta K}{\delta \phi_k}$$

To make things easier, for now assume the orbitals are real valued $\phi_k^* = \phi_k$

Start with the most straightforward term, the potential energy

$$V[\phi] = \sum_i^n \int v(\mathbf{r}_1)\phi_i^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1)\, d\mathbf{x}_1$$

Reminder $$\frac{\delta F}{\delta f} = \frac{\partial F}{\partial f} - \nabla \cdot \frac{\partial F}{\partial \nabla f} + \nabla^2 \frac{\partial F}{\partial \nabla^2 f} - \dots$$

Applying the formula

$$\frac{\delta V}{\delta \phi_k}(\mathbf{x}) = \frac{\partial V}{\partial \phi_k(\mathbf{x})} = 2v(\mathbf{r})\phi_k(\mathbf{x})$$

The functional derivative of the kinetic energy

We need the functional derivative of the energy with repect to a change in one of the orbitals ϕ_k

$$\frac{\delta E}{\delta \phi_k} = \frac{\delta T}{\delta \phi_k} + \frac{\delta V}{\delta \phi_k} + \frac{\delta J}{\delta \phi_k} - \frac{\delta K}{\delta \phi_k}$$

The kinetic energy term is

$$T[\phi] = \sum_i^n \int -\frac{1}{2}\phi_i^*(\mathbf{x}_1)\nabla^2\phi_i(\mathbf{x}_1)\, d\mathbf{x}_1$$

Reminder $\quad \frac{\delta F}{\delta f} = \frac{\partial F}{\partial f} - \nabla \cdot \frac{\partial F}{\partial \nabla f} + \nabla^2 \frac{\partial F}{\partial \nabla^2 f} - \dots$

Apply the formula (assuming $\phi_k^* = \phi_k$)

$$\begin{aligned}\frac{\delta T}{\delta \phi_k}(\mathbf{x}) = \frac{\partial T}{\partial \phi_k(\mathbf{x})} + \nabla^2 \frac{\partial T}{\partial \nabla^2 \phi_k(\mathbf{x})} &= -\frac{1}{2}\nabla^2\phi_k(\mathbf{x}) - \frac{1}{2}\nabla^2\phi_k(\mathbf{x}) \\ &= -\nabla^2\phi_k(\mathbf{x})\end{aligned}$$

The functional derivative of the Coulomb energy

The Coulomb energy is

$$J[\phi] = \frac{1}{2}\sum_{ij}^{n} \int\int \phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2$$

Applying the formula (assuming $\phi_k^* = \phi_k$)

$$\begin{aligned}\frac{\delta J}{\delta \phi_k}(\mathbf{x}) &= \frac{\partial}{\partial \phi_k(\mathbf{x})}\frac{1}{2}\sum_{ij}^{n} \int\int \phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2 \\ &= \sum_{i}^{n} \int \frac{|\phi_i(\mathbf{x}_1)|^2}{|\mathbf{r}-\mathbf{r}_1|}\, d\mathbf{x}_1 \phi_k(\mathbf{x}) + \sum_{j}^{n} \int \frac{|\phi_j(\mathbf{x}_2)|^2}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{x}_2 \phi_k(\mathbf{x}) \\ &= 2\sum_{j}^{n} \int \frac{|\phi_j(\mathbf{x}_2)|^2}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{x}_2 \phi_k(\mathbf{x}) = 2\int \frac{\rho(\mathbf{x}_2)}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{x}_2 \phi_k(\mathbf{x})\end{aligned}$$

The functional derivative of the exchange energy

The exchange energy is

$$K[\phi] = \frac{1}{2}\sum_{ij}^{n} \int\!\!\int \phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\phi_j(\mathbf{x}_1)\phi_i(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2$$

Applying the formula (assuming $\phi_k^* = \phi_k$)

$$\begin{aligned}
\frac{\delta K}{\delta \phi_k}(\mathbf{x}) &= \frac{\partial}{\partial \phi_k(\mathbf{x})}\frac{1}{2}\sum_{ij}^{n} \int\!\!\int \phi_i^*(\mathbf{x}_1)\phi_j^*(\mathbf{x}_2)\frac{1}{r_{12}}\phi_j(\mathbf{x}_1)\phi_i(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2 \\
&= \sum_{i}^{n} \int \frac{\phi_i(\mathbf{x}_1)\phi_k(\mathbf{x}_1)}{|\mathbf{r}-\mathbf{r}_1|}\, d\mathbf{x}_1 \phi_i(\mathbf{x}) + \sum_{j}^{n} \int \frac{\phi_j(\mathbf{x}_2)\phi_k(\mathbf{x}_2)}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{x}_2 \phi_j(\mathbf{x}) \\
&= 2\sum_{j}^{n} \int \frac{\phi_j(\mathbf{x}_2)\phi_k(\mathbf{x}_2)}{|\mathbf{r}-\mathbf{r}_2|}\, d\mathbf{x}_2 \phi_j(\mathbf{x})
\end{aligned}$$

The functional derivative of the Hartree–Fock energy

Putting it all together, the functional derivative of the energy with repect to a change in one of the orbitals ϕ_k is

$$\begin{aligned}\frac{\delta E}{\delta \phi_k} &= \frac{\delta T}{\delta \phi_k} + \frac{\delta V}{\delta \phi_k} + \frac{\delta J}{\delta \phi_k} - \frac{\delta K}{\delta \phi_k} \\ &= 2\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \hat{J} - \hat{K}\right)\phi_k(\mathbf{x})\end{aligned}$$

We have introduced the Coulomb and exchange potential operators

$$\hat{J}\phi_k(\mathbf{x}) = \sum_j^n \int \frac{\phi_j^*(\mathbf{x}')\phi_j(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{x}' \phi_k(\mathbf{x})$$

$$\hat{K}\phi_k(\mathbf{x}) = \sum_j^n \int \frac{\phi_j^*(\mathbf{x}')\phi_k(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{x}' \phi_j(\mathbf{x})$$

The Fock equation

The Fock equation results from the stationary condition for minimising the energy of a Slater determinant wavefunction

$$\begin{aligned} L[\phi] =& E[\phi] - \sum_{ij} \epsilon_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right) \\ \frac{\delta L}{\delta \phi_k}(\mathbf{x}) =& \frac{\delta E}{\delta \phi_k}(\mathbf{x}) - 2 \sum_j \epsilon_{kj} \phi_j(\mathbf{x}) = 0 \end{aligned}$$

The matrix of multipliers ϵ_{ij} is hermitian. The canonical Hartree–Fock orbitals are those that diagonalise $\epsilon_{ij} = \epsilon_i \delta_{ij}$.

$$\hat{F} \phi_k(\mathbf{x}) = \epsilon_k \phi_k(\mathbf{x}) \qquad \text{Canonical Fock equation}$$

$$\hat{F} = -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \hat{J} - \hat{K} \qquad \text{Fock operator}$$

The orbitals that minimise the energy of a Slater determinant are eigenfunctions of the Fock operator. The eigenvalues ϵ_k are orbital energies.

Self-consistent solution

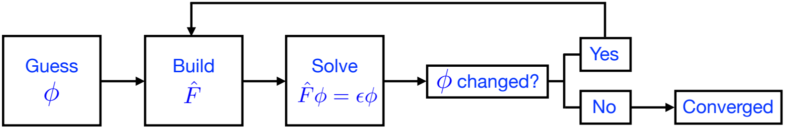
The eigenfunctions of $\hat{F}$ form a complete one-electron basis $\{\phi_p\}$. The n lowest energy orbitals are occupied $\{\phi_i\}$ the rest are virtual orbitals $\{\phi_a\}$.

$$\hat{F}\phi_p(\mathbf{x}) = \epsilon_p \phi_p(\mathbf{x}) \qquad \text{Canonical Fock equation}$$

$$\hat{F} = -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \hat{J} - \hat{K} \qquad \text{Fock operator}$$

$\hat{F}$ is a one electron operator accounting for the kinetic energy and effective potential energy. Together, the Coulomb and exchange operators exert the net repulsion due to all of the other electrons.

Since $\hat{J}$ and $\hat{K}$ depend on the orbitals, the equations must be solved iteratively. This is known as self-consistent-field theory.



Koopman's Theorems

Koopman provided a physical interpretation of the orbital eigenvalues

Consider either removing an electron from an occupied orbital ϕ_i or adding an electron to a virtual orbital ϕ_a, while the orbitals remain unchanged.

Occupied orbital eigenvalues are the negative of the ionisation potentials

$$E_i^+ - E = -\langle\varphi_i|\hat{h}_1|\varphi_i\rangle - \sum_j^n \left(\langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_i\varphi_j\rangle - \langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_j\varphi_i\rangle\right) = -\epsilon_i$$

Virtual orbital eigenvalues are the electron affinities

$$E_a^- - E = \langle\varphi_a|\hat{h}_1|\varphi_a\rangle + \sum_j^n \left(\langle\varphi_a\varphi_j|r_{12}^{-1}|\varphi_a\varphi_j\rangle - \langle\varphi_a\varphi_j|r_{12}^{-1}|\varphi_j\varphi_a\rangle\right) = \epsilon_a$$

Predictions of IPs and EAs using Hartree–Fock theory benefit from a favourable cancellation of missing correlation and missing orbital relaxation

Restricted Hartree–Fock Theory

The constraint that the α and β spin-orbitals share the same spatial functions is called Restricted Hartree–Fock theory

$$|\psi\rangle = \sqrt{n!}\,\hat{A}\,|\varphi_1\alpha \ldots \varphi_{n_\alpha}\alpha\,\varphi_1\beta \ldots \varphi_{n_\beta}\beta\rangle$$

Spin-restriction is advantageous

- Same Fock equation for the α and β spin orbitals
- The wavefunction is an eigenfunction of $\hat{S}_z$
  - and therefore also of $\hat{S}^2$ when $M_s = S$

When $n_\alpha = n_\beta = n/2$ the energy expression reduces to

$$E = 2\sum_{i}^{n/2}\langle\varphi_i|\hat{h}_1|\varphi_i\rangle + \sum_{ij}^{n/2}\big(2\langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_i\varphi_j\rangle - \langle\varphi_i\varphi_j|r_{12}^{-1}|\varphi_j\varphi_i\rangle\big)$$

Matrix equations

The Fock equation is converted to a matrix equation by expanding the n unknown orbitals ϕ_k in a basis of $m > n$ predefined orbitals $\chi_u(\mathbf{x})$

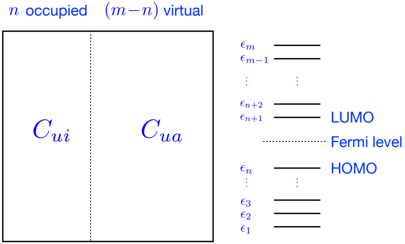
$$\phi_k(\mathbf{x}) = \sum_u^m \chi_u(\mathbf{x}) C_{uk}$$

Projection into the basis gives the Roothaan–Hall equations

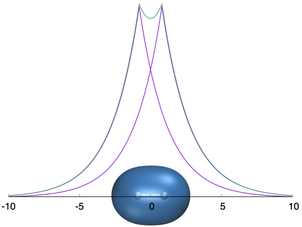
$$\sum_v^m \langle \chi_u | \hat{F} | \chi_v \rangle C_{vk} = \sum_v^m \langle \chi_u | \chi_v \rangle C_{vk} \epsilon_k$$

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}$$

m AOs $\longrightarrow$ m MOs



LCAO approach



ϕ behaves like an AO near each nucleus

$$\phi_k(\mathbf{x}) = \sum_u^m \chi_u(\mathbf{x}) C_{uk}$$

Each $\chi_u(\mathbf{x})$ is an AO centred on one of the atoms

Practical calculations require the definition of a good orbital basis

- Complete: systematic convergence to the exact orbitals
- Suitable: accurate orbital are obtained with few functions
- Tractable: Fock and overlap matrices can be evaluated easily
    - Hydrogenic functions: difficult integrals, complete if add continuum
    - Use Gaussian-type Atomic Orbitals

Gaussian-type atomic orbitals

Gaussian-type AOs that mimic hydrogenic orbitals are formed from linear combinations of (normalised) primitive Cartesian Gaussians

Primitive Cartesian GTOs raw functions with easy integral formulas

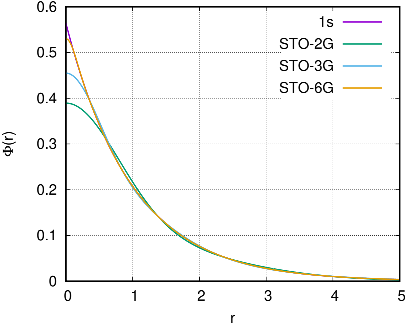
$$\chi_{v,\mathbf{l}}(\mathbf{r}) = N_{v,\mathbf{l}}\,(x - A_x)^{l_x}(y - A_y)^{l_y}(z - A_z)^{l_z}\exp(-\alpha_v r^2)$$

Contracted Cartesian GTO
emulate exponential functions

$$\chi_{u,\mathbf{l}}(\mathbf{r}) = \sum_i \chi_{v,\mathbf{l}}(\mathbf{r})\, c_{vu}$$

Real Spherical GTO
emulate hydrogenic functions

$$\chi_{u,lm}(\mathbf{r}) = \sum_{l,m,n} \chi_{u,\mathbf{l}}(\mathbf{r})\, C_{\mathbf{l},lm}$$



Integrals

Gaussian functions are convenient because the overlap and Fock matrix integrals are easy to compute

Gaussian Product Theorem: The product of two Gaussians is a Gaussian

$$e^{-\alpha(\mathbf{r}-\mathbf{A})^2} e^{-\beta(\mathbf{r}-\mathbf{B})^2} = e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{C})^2}, \qquad \mathbf{C} = \frac{\alpha\mathbf{A}+\beta\mathbf{B}}{\alpha+\beta}$$

e.g. Overlap between two s functions on atoms at **A** and **B**

$$\int e^{-\alpha(\mathbf{r}-\mathbf{A})^2} e^{-\beta(\mathbf{r}-\mathbf{B})^2}\, d\mathbf{r} = e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} \left(\frac{\pi}{\alpha+\beta}\right)^{3/2}$$

Integrals for p and d functions etc are generated by differentiating with respect to the atomic centres A and B.

e.g. Electron repulsion integrals via integral transformation (complicated)

$$\iint r_{12}^{-1} e^{-\alpha(\mathbf{r}_1-\mathbf{A})^2} e^{-\beta(\mathbf{r}_2-\mathbf{B})^2}\, d\mathbf{r}_1\mathbf{r}_2 = \left(\frac{\pi^2}{\alpha\beta}\right)^{3/2} R_{AB}^{-1}\,\mathrm{erf}(\omega R_{AB}) \quad \omega = \sqrt{\frac{\alpha\beta}{\alpha+\beta}}$$

Basis sets

The minimal STO-*n*G basis sets only have one function per occupied AO

Systematically add flexibility to represent different atomic environments:

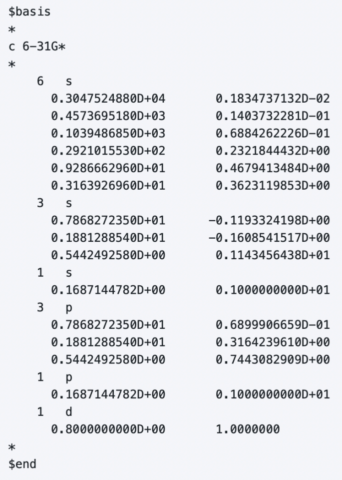
- 2 (SV,DZ), 3 (TZ), 4 (QZ) etc functions per valence orbital
- polarisation functions (*,p) allow for distortion of valence orbitals
- diffuse functions (+,aug) improve orbital tails (e.g. for anions)

Optimised to give same % accuracy for every atom in periodic table

Examples	**DZ**	**TZ**
polarisation (not H)	6-31G*, SV(P)	6-311G*
polarisation (all)	6-31G**, SVP, cc-pVDZ	6-311G**, TZVP, cc-pVTZ
diffuse fun. (not H)	6-31+G**	6-311+G**
diffuse fun. (all)	6-31++G**, aug-cc-pVDZ	6-311++G**, aug-cc-pVTZ

Pseudo potentials for atoms heavier than Ar where core electrons are swapped for an effective potential to account for relativistic effects

Basis set example: 6-31G* for carbon

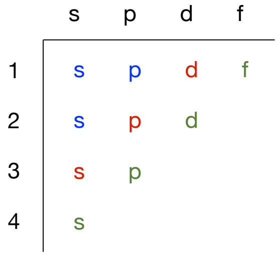


```
$basis
*
c 6-31G*
*
    6   s
      0.3047524880D+04        0.1834737132D-02
      0.4573695180D+03        0.1403732281D-01
      0.1039486850D+03        0.6884262226D-01
      0.2921015530D+02        0.2321844432D+00
      0.9286662960D+01        0.4679413484D+00
      0.3163926960D+01        0.3623119853D+00
    3   s
      0.7868272350D+01       -0.1193324198D+00
      0.1881288540D+01       -0.1608541517D+00
      0.5442492580D+00        0.1143456438D+01
    1   s
      0.1687144782D+00        0.1000000000D+01
    3   p
      0.7868272350D+01        0.6899906659D-01
      0.1881288540D+01        0.3164239610D+00
      0.5442492580D+00        0.7443082909D+00
    1   p
      0.1687144782D+00        0.1000000000D+01
    1   d
      0.8000000000D+00        1.0000000
*
$end
```

Basis set hierarchy follows the general pattern

DZ : 3s2p1f

TZ : 4s3p2f1d

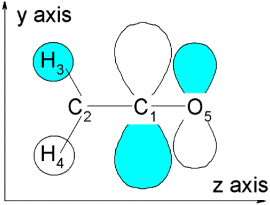


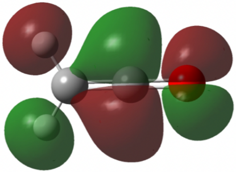
	s	p	d	f
1	s	p	d	f
2	s	p	d	
3	s	p		
4	s			

Basis Set Exchange https://www.basissetexchange.org

Molecular orbital visualisation

A typical output from a Hartree–Fock calculation is a list of atomic orbital coefficients C_{uk} that can be visualised to interpret bonding and reactivity





AO no.	Atom no.	Atom	AO	c_{ij}	c_{ij}	c_{ij}
			MO no.	10	11	12
			Symmetry	(B2)	(B1)	(B2)
			Energy	-0.43167	-0.27366	0.23960
1	1	C	1S	0.00000	0.00000	0.00000
2			2S	0.00000	0.00000	0.00000
3			2PX	0.00000	0.34701	0.00000
4			2PY	0.46426	0.00000	0.83392
5			2PZ	0.00000	0.00000	0.00000
6	2	C	1S	0.00000	0.00000	0.00000
7			2S	0.00000	0.00000	0.00000
8			2PX	0.00000	0.71070	0.00000
9			2PY	-0.22197	0.00000	0.08041
10			2PZ	0.00000	0.00000	0.00000
11	3	H	1S	-0.21172	0.00000	-0.26529
12	4	H	1S	0.21172	0.00000	0.26529
13	5	O	1S	0.00000	0.00000	0.00000
14			2S	0.00000	0.00000	0.00000
15			2PX	0.00000	-0.58631	0.00000
16			2PY	0.72589	0.00000	-0.67027
17			2PZ	0.00000	0.00000	0.00000

Mulliken population analysis

The charge from an orbital ϕ_i is distributed between atomic orbitals

$$1 = \langle \phi_i | \phi_i \rangle = \sum_{uv} C^*_{ui} S_{uv} C_{vi} = \sum_{uv} P^i_{uv} \qquad \text{population matrix}$$

Overlap population P^i_{uv}: > 0 bonding; < 0 anti-bonding; 0 non-bonding.

The total population in AO u from orbital i is $P^i_u = \sum_v P^i_{uv}$

The gross atomic population is $P_I = \sum_{u \in I} \sum_i P^i_u$

Atomic partial charges q_I quanitfy charge separation in molecules due to atoms with different electronegativities

$$q_I = Z_I - P_I \qquad \text{Mulliken charges}$$

Caveat: Mulliken charges become ill-defined for large basis sets

Properties

Electrostatic moments, such as the electronic dipole and quadrupole moments are obtained as expectation values

$$\mathbf{u} = \langle\psi|\hat{\mathbf{u}}|\psi\rangle = \sum_i \langle\phi_i|\hat{\mathbf{u}}|\phi_i\rangle$$

The forces on the atoms are obtained by differentiating the Lagrangian

$$\mathbf{F}_I = -\nabla_I L[\phi]$$

Force constants and vibrational frequencies require the second derivatives

Hartree–Fock theory can be used to find equilbrium structures of molecules, transition states that connect reaction species, and compute the thermodynamic and kinetic parameters, as well as spectroscopic signatures.

Accuracy of Hartree–Fock theory

The potential energy surface is often qualitatively correct and chemical phenomena are in many cases well characterised, but quantitative agreement with experiment is rarely found

- Thermochemistry
  - Dissociation energies are too small (F2 is not predicted to exist!)
  - Reaction barrier heights are much too high
  - Dispersion effects are completely absent
- Properties:
  - Bond lengths typically 0.02 Å too short
  - Frequencies 10% too large
  - Dipole moments 10% too large

Failures of Hartree–Fock theory

Hartree–Fock theory is qualitatively wrong for electronic states that are resonant among multiple electronic configurations.

- e.g. Be: Ψ is a superposition of $1s^2 2s^2$ and $1s^2 2p^2$ multi-reference

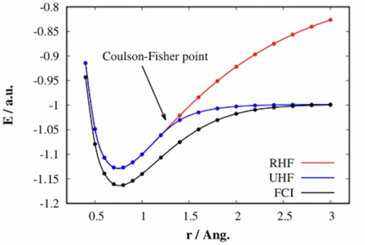
Hartree–Fock theory fails for bond breaking $\left[|\sigma_g \sigma_g\rangle = 2\hat{A}|\sigma_g \alpha \sigma_g \beta\rangle\right]$

- Unphysical ionic character leads to too high energy: e.g. dissociated H_2

$$\sigma_g = \sqrt{\tfrac{1}{2}}\left(s_A + s_B\right)$$

$$|\sigma_g \sigma_g\rangle = \tfrac{1}{2}\Big(\underbrace{|s_A s_A\rangle + |s_B s_B\rangle}_{\text{ionic}} + \underbrace{|s_A s_B\rangle + |s_B s_A\rangle}_{\text{covalent}}\Big)$$

$$|\Psi\rangle = \sqrt{\tfrac{1}{2}}\left(|s_A s_B\rangle + |s_B s_A\rangle\right)$$



The symmetry-broken unrestricted Hartree–Fock wavefunction $|s_A s_B\rangle$ has the correct energy, but incorrect properties e.g. $\hat{S}^2|\psi\rangle \neq S(S+1)|\psi\rangle$

Electron Correlation

Aim: Solve $\hat{H}\Psi_k = E_k\Psi_k$ exactly, accounting for many-body correlation

Expand the unknown Ψ in a basis of known functions f_I

$$\Psi_k(\mathbf{x}_1, \ldots, \mathbf{x}_n) = \sum_I f_I(\mathbf{x}_1, \ldots, \mathbf{x}_n) C_{Ik}$$

Schrödinger equation becomes a matrix equation in a finite Hilbert space

$$\sum_J H_{IJ} C_{Jk} = \sum_J S_{IJ} C_{Jk} E_k \qquad \begin{aligned} H_{IJ} &= \langle f_I | \hat{H} | f_J \rangle \\ S_{IJ} &= \langle f_I | f_J \rangle \end{aligned}$$

Practical calculations require a good basis f_I

- Complete: systematic convergence to the exact wavefunction
- Suitable: accurate energies are obtained with few functions
- Tractable: Hamiltonian and overlap matrices can be evaluated easily

Exact Conditions

Aim: Solve $\hat{H}\Psi_k = E_k\Psi_k$ exactly, accounting for many-body correlation

$$\Psi_k(\mathbf{x}_1, \ldots, \mathbf{x}_n) = \sum_I f_I(\mathbf{x}_1, \ldots, \mathbf{x}_n) C_{Ik}$$

Impose exact conditions on Ψ on each f_I

Exact condition 1 If $\hat{H}\Psi = E\Psi$ and $[\hat{H}, \hat{A}] = 0$, then $\hat{A}\Psi = a\Psi$

The exact wavefunction is also an eigenfunction of any operator that commutes with the Hamiltonian.

Fermionic antisymmetry is obeyed	$\hat{\pi}_\mu \Psi = (-1)^{p_\mu}\Psi$	✓
Spin is a good quantum number	$\hat{S}^2\Psi = S(S+1)\Psi$	✓
Spin polarisation is a good quantum number	$\hat{S}_z\Psi = M_s\Psi$	✓
Molecular point group symmetry is obeyed	$\hat{O}\Psi = o\Psi$	✓

Slater determinants are a good choice $|f_I\rangle = \sqrt{n!}\,\hat{A}\,|\phi_1 \cdots \phi_n\rangle$

Exact Conditions

Aim: Solve $\hat{H}\Psi_k = E_k \Psi_k$ exactly, accounting for many-body correlation

$$\Psi_k(\mathbf{x}_1, \ldots, \mathbf{x}_n) = \sum_I f_I(\mathbf{x}_1, \ldots, \mathbf{x}_n) C_{Ik}$$

Impose exact conditions on Ψ on each f_I

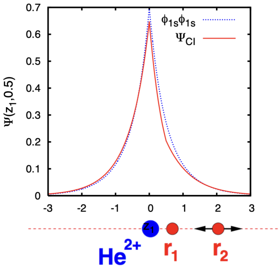
Exact condition 2 Kato's cusp conditions

Divergences in the Coulomb energy at charged particle coalescence points must be exactly cancelled by divergences in the kinetic energy

$$\left.\frac{\partial \Psi}{\partial r_{iI}}\right|_{r_{iI}=0} = -Z_I \Psi\Big|_{r_{iI}=0} \qquad \text{e-n cusp}$$

$$\left.\frac{\partial \Psi}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\Psi\Big|_{r_{12}=0} \qquad \text{e-e cusp}$$

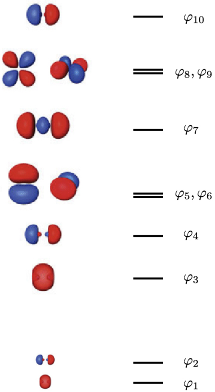
e-n cusp condition applies to each orbital ϕ in $|f_I\rangle = \sqrt{n!}\,\hat{A}\,|\phi_1 \cdots \phi_n\rangle$



Configuration Interaction Theory

Expand Ψ using all possible configurations of n electrons in the Hartree–Fock orbitals $$|\Psi_k\rangle = \sum_{\mathbf{P}} |\mathbf{P}\rangle C_{Pk}$$

Configuration The Slater determinant wavefunction associated with an orbital occupancy $|\mathbf{P}\rangle = \sqrt{n!}\,\hat{A}\,|\phi_{P_1}\phi_{P_2}\ldots\phi_{P_n}\rangle$



e.g. He$_2$:

$$1\sigma_g^2 1\sigma_u^2 : \quad \sqrt{n!}\,\hat{A}\,|\varphi_1\alpha\varphi_2\alpha\varphi_1\beta\varphi_2\beta\rangle$$

$$1\sigma_g^2 2\sigma_g^{\uparrow}\pi_{u,x}^{\downarrow} : \quad \sqrt{n!}\,\hat{A}\,|\varphi_1\alpha\varphi_3\alpha\varphi_1\beta\varphi_5\beta\rangle$$

Hartree–Fock theory performed in a basis of m AOs provides m MOs

$\binom{m}{n_\alpha} \times \binom{m}{n_\beta}$ configurations

Completeness

Eigenfunctions of the Fock operator form a complete one-electron basis

$$\hat{F}\phi_p = \epsilon_p \phi_p \qquad \underbrace{\phi_1 \phi_2 \dots \phi_n}_{\text{occupied } \phi_i} \; \underbrace{\phi_{n+1} \dots \phi_\infty}_{\text{virtual } \phi_a}$$

Arbitrary orbital shapes can be expressed in the basis $f(\mathbf{x}) = \sum_p \phi_p(\mathbf{x}) C_p$

All possible products of n spin orbitals forms a complete n-electron basis

$$\sqrt{n!}\hat{A}|\phi_{P_1}(\mathbf{x}_1)\phi_{P_2}(\mathbf{x}_2)\dots\phi_{P_n}(\mathbf{x}_n)\rangle$$

By increasing the AO basis and taking all possible configurations, the exact wavefunction can be obtained to arbitrary accuracy, at least in principle.

Tractability: the Slater–Condon rules

Slater Determinants have tractable matrix elements

$$\langle \mathbf{P}|\mathbf{Q}\rangle = \delta_{\mathbf{PQ}} \qquad \text{orthonormal}$$

$$\langle \mathbf{P}|\hat{H}|\mathbf{Q}\rangle = 0 \qquad \text{unless } \mathbf{P}, \mathbf{Q} \text{ share } n-2 \text{ orbitals}$$

The non-zero elements for one-electron and two-electron operators are

$$n!\langle \phi_1 \ldots \phi_n|\hat{A}\hat{h}\hat{A}|\phi_1 \ldots \phi_n\rangle = \sum_i^n \langle \phi_i|\hat{h}_1|\phi_i\rangle$$

$$n!\langle \phi_1 \ldots \phi_a \ldots \phi_n|\hat{A}\hat{h}\hat{A}|\phi_1 \ldots \phi_i \ldots \phi_n\rangle = \langle \phi_a|\hat{h}_1|\phi_i\rangle$$

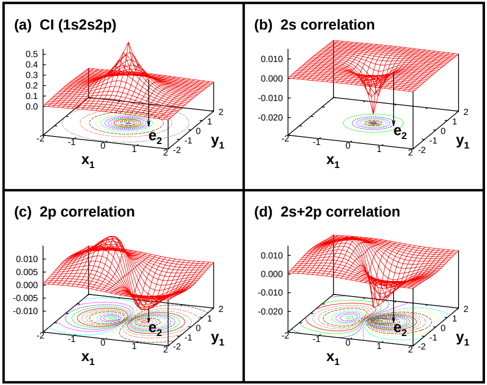
$$n!\langle \phi_1 \ldots \phi_n|\hat{A}\hat{g}\hat{A}|\phi_1 \ldots \phi_n\rangle = \frac{1}{2}\sum_{ij}^n \langle \phi_i\phi_j|r_{12}^{-1}|\phi_i\phi_j\rangle - \langle \phi_i\phi_j|r_{12}^{-1}|\phi_j\phi_i\rangle$$

$$n!\langle \phi_1 \ldots \phi_a \ldots \phi_n|\hat{A}\hat{g}\hat{A}|\phi_1 \ldots \phi_i \ldots \phi_n\rangle = \sum_j^n \langle \phi_a\phi_j|r_{12}^{-1}|\phi_i\phi_j\rangle - \langle \phi_a\phi_j|r_{12}^{-1}|\phi_j\phi_i\rangle$$

$$n!\langle \phi_1 \ldots \phi_a\phi_b \ldots \phi_n|\hat{A}\hat{g}\hat{A}|\phi_1 \ldots \phi_i\phi_j \ldots \phi_n\rangle = \langle \phi_a\phi_b|r_{12}^{-1}|\phi_i\phi_j\rangle - \langle \phi_a\phi_b|r_{12}^{-1}|\phi_j\phi_i\rangle$$

Lessons from helium

Radial and angular correlation in $|\Psi\rangle$


(a) CI (1s2s2p)

(b) 2s correlation

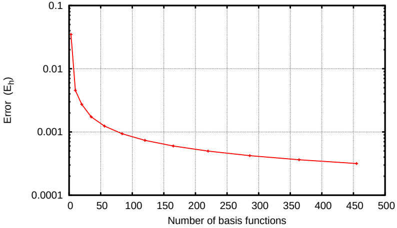
(c) 2p correlation

(d) 2s+2p correlation

(a) $|\Psi\rangle$ (b,c,d) $|\Psi\rangle - |1s1s\rangle$ corr. hole

$$|\Psi\rangle = C_1|1s1s\rangle + C_2|1s2s\rangle + C_3|2s2s\rangle + C_4(|2p_x2p_x\rangle + |2p_y2p_y\rangle + |2p_z2p_z\rangle)$$

Slow convergence with AO basis



$$E - E_{\text{exact}} \propto N^{-1}$$
$$\propto X^{-3}$$

N is size of AO basis

X is Cardinal number

- CI requires large correlation adapted AO basis sets due to e-e cusp

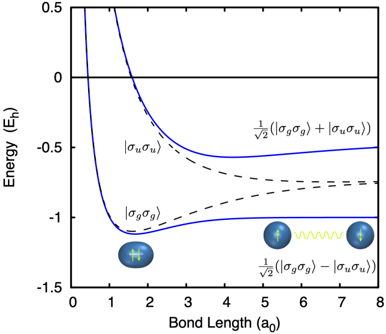
Static and Dynamic correlation

Weakly correlated states are characterised by CI expansions with one large coefficient, the HF determinant

- The correlation processes are typically dynamic in nature

Strongly correlated states are characterised by CI expansions with two or more large coefficients

- The correlation processes are often static in nature



e.g. H_2: weakly correlated at equilibrium, strongly correlated at stretched geometries

$$|\Psi\rangle_{\text{eq}} = 0.98|\sigma_g\sigma_g\rangle - 0.14|\sigma_u\sigma_u\rangle$$

$$|\Psi\rangle_{\text{dis}} = \frac{1}{\sqrt{2}}\Big(|\sigma_g\sigma_g\rangle - |\sigma_u\sigma_u\rangle\Big)$$

$$= \frac{1}{\sqrt{2}}\Big(|s_A s_B\rangle + |s_B s_A\rangle\Big)$$

Near degeneracy leads to strong mixing

Practical considerations

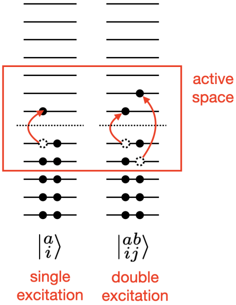
Full configuration interaction calculations are impossible beyond 10 electrons in 30 orbitals $\binom{30}{5} \times \binom{30}{5} = 2 \times 10^{10}$ 160 Gb

Cannot perform large basis set FCI calculations must make approximations

- Truncated CI based on excitation rank

$$|\Psi\rangle = |\mathrm{HF}\rangle C_0 + \sum_{ia} |{}^a_i\rangle C_i^a + \sum_{ijab} |{}^{ab}_{ij}\rangle C_{ij}^{ab} + \dots$$

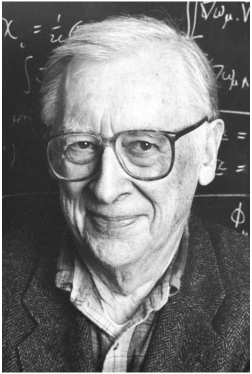
- Truncated CI based on active space CAS
- Perturbation theory MP2, MP3 ...
- Truncated exponential parameterisation (coupled-cluster) CCSD, CCSDT ...



Treatment of electron correlation through wavefunction expansions is much more computationally expensive than HF theory

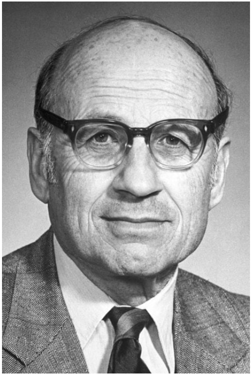
1998 Nobel prize

John Pople



"for his development of computational methods in quantum chemistry"

Walter Kohn



"for his development of the density-functional theory"

Density Functional Theory

Hohenberg and Kohn proved that it is formally possible to use the electron density $\rho(\mathbf{r})$ instead of the wavefunction to find ground state energies

$$E_0 = \min_{\Psi} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \longrightarrow \quad E_0 = \min_{\rho} E[\rho]$$

Recall $\rho(\mathbf{r}) = n \int \Psi^*(\mathbf{x}, \mathbf{x}_2 \ldots \mathbf{x}_n) \Psi(\mathbf{x}, \mathbf{x}_2 \ldots \mathbf{x}_n) ds d\mathbf{x}_2 \ldots d\mathbf{x}_n$

This is a remarkable simplification

- $\Psi(\mathbf{x}, \mathbf{x}_2 \ldots \mathbf{x}_n)$ 4n degrees of freedom (complicated)
- $\rho(\mathbf{r})$ 3 degrees of freedom (simple)

Caveat: the true density fuctional $E[\rho]$ is unknown.

DFT makes use of approximations to $E[\rho]$

Density Functional Theory

Hohenberg and Kohn proved that it is formally possible to use the electron density $\rho(\mathbf{r})$ instead of the wavefunction to find ground state energies

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- Prove that the energy functional $E[\rho]$ formally exists (HK I)
- Prove the varitional principle $E[\rho] \geq E_0$ (HK II)
- Practical method for optimising ρ (Kohn–Sham theory)
- Find good approximations for $E[\rho]$ (next lecture)

Hohenberg–Kohn I

The ground state density $\rho(\mathbf{r})$ fully determines the Hamiltonian.

$$\rho \longrightarrow \hat{H} \longrightarrow E, \Psi$$

$\therefore E[\rho]$ exists: *if you have $\rho(\mathbf{r})$, then you can find $\hat{H}$ and therefore E*

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V} = \hat{\mathcal{F}} + \hat{V}$$

$$\hat{\mathcal{F}} = \sum_i^n -\frac{1}{2}\nabla_i^2 + \sum_{i>j}^n \frac{1}{r_{ij}}$$ universal, depends only on n

$$\hat{V} = \sum_i^n v(\mathbf{r}_i) = -\sum_{iI}^{nN} \frac{Z_I}{r_{iI}}$$ molecule specific

$n = \int \rho(\mathbf{r})\, d\mathbf{r}$. Thus $\rho(\mathbf{r})$ determines n and therefore $\hat{\mathcal{F}}$.

The nuclear positions and charges can be found from the cusps in $\rho(\mathbf{r})$

$$\left.\frac{\partial \rho(\mathbf{R}_I + \mathbf{r})}{\partial r}\right|_{r=0} = -2Z_I \rho(\mathbf{R}_I)$$ Kato cusp condition

Hohenberg–Kohn I: proof by contradiction

Suppose that $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ give the same ρ. Then $\rho \not\to \hat{H}$

$$\hat{H}_1 = \hat{\mathcal{F}} + \hat{V}_1 \qquad \hat{H}_1|\Psi_1\rangle = E_1|\Psi_1\rangle \qquad \Psi_1 \to \rho_1(\mathbf{r}) = \rho(\mathbf{r})$$

$$\hat{H}_2 = \hat{\mathcal{F}} + \hat{V}_2 \qquad \hat{H}_2|\Psi_2\rangle = E_2|\Psi_2\rangle \qquad \Psi_2 \to \rho_2(\mathbf{r}) = \rho(\mathbf{r})$$

Step 1: if $\Psi_1 = \Psi_2 = \Psi$ then

$$(\hat{H}_1 - \hat{H}_2)|\Psi\rangle = (\hat{V}_1 - \hat{V}_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle$$

This can only be true if $\hat{V}_1 = \hat{V}_2 + \text{const}$. Therefore $\Psi_1 \neq \Psi_2$.

Step 2: By the variational principle $E_1 + E_2 < E_2 + E_1$ contradiction

$$E_1 < \langle\Psi_2|\hat{H}_1|\Psi_2\rangle \qquad E_2 < \langle\Psi_1|\hat{H}_2|\Psi_1\rangle$$

$$E_1 < \langle\Psi_2|\hat{H}_2 + \hat{V}_1 - \hat{V}_2|\Psi_2\rangle \qquad E_2 < \langle\Psi_1|\hat{H}_1 - \hat{V}_1 + \hat{V}_2|\Psi_1\rangle$$

$$E_1 < E_2 + \int (v_1(\mathbf{r}) - v_2(\mathbf{r}))\rho(\mathbf{r})\,d\mathbf{r} \qquad E_2 < E_1 - \int (v_1(\mathbf{r}) - v_2(\mathbf{r}))\rho(\mathbf{r})\,d\mathbf{r}$$

Different molecules cannot have the same ground state density.

Therefore $\rho(\mathbf{r}) \longrightarrow v(\mathbf{r}) + \text{const}$ and therefore $E[\rho]$ exists.

Hohenberg–Kohn II (as redefined by Levy and Leib)

The variational energy functional is

$$E_0 \leq E[\rho] = F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \qquad \text{Universal functional } F[\rho]$$

Derivation: Rewrite search over normalised n-electron Ψ by partitioning the full set of Ψ into subsets containing Ψ that have the same density.

$$\begin{aligned} E_0 &= \min_{\Psi} \langle \Psi | \hat{\mathcal{F}} + \hat{V} | \Psi \rangle \\ &= \min_{\rho} \min_{\Psi \to \rho} \langle \Psi | \hat{\mathcal{F}} + \hat{V} | \Psi \rangle \\ &= \min_{\rho} \left\{ \min_{\Psi \to \rho} \langle \Psi | \hat{\mathcal{F}} | \Psi \rangle + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \right\} \\ &= \min_{\rho} \left\{ F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \right\} \end{aligned}$$

n-representability: ρ must come from a valid n-electron wavefunction

Kohn–Sham theory

- Introduce a ficticious system of n non-interacting electrons and a non-interacting kinetic energy functional $T_s[\rho]$

$$|\Phi_s\rangle = \sqrt{n!}\,\hat{A}\,|\phi_1 \ldots \phi_n\rangle \qquad \text{Kohn–Sham determinant}$$

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \qquad \text{exchange-correlation functional}$$

$$T_s[\rho] = \min_{\Phi_s \to \rho} \langle \Phi_s | \hat{T} | \Phi_s \rangle$$

- Search over n-representable ρ by searching over Φ_s

$$\begin{aligned}
E_0 &= \min_{\rho} \left\{ T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} \right\} \\
&= \min_{\rho} \min_{\Phi_s \to \rho} \left\{ \langle \Phi_s | \hat{T} + \hat{V} + \hat{J} | \Phi_s \rangle + E_{xc}[\rho] \right\} \\
&= \min_{\Phi_s} \left\{ \langle \Phi_s | \hat{T} + \hat{V} + \hat{J} | \Phi_s \rangle + E_{xc}[\rho_\Phi] \right\} \qquad \text{Kohn–Sham energy}
\end{aligned}$$

Kohn–Sham equations

Optimise the Kohn–Sham Lagrangian

$$L[\phi] = T_s[\phi] + V[\phi] + J[\phi] + E_{xc}[\phi] - \sum_{ij} \epsilon_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$

$$\frac{\delta L}{\delta \phi_k(\mathbf{x})} = 2 \left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \hat{J} \right) \phi_k(\mathbf{x}) + \frac{\delta E_{xc}}{\delta \phi_k(\mathbf{x})} - 2 \sum_{kj} \epsilon_{kj} \phi_j(\mathbf{x}) = 0$$

Use the chain rule $\displaystyle\frac{\delta E_{xc}}{\delta \phi_k(\mathbf{x})} = \int \frac{\delta E_{xc}}{\delta \rho(\mathbf{x}')} \frac{\delta \rho(\mathbf{x}')}{\delta \phi_k(\mathbf{x})} \, d\mathbf{x}'$

$$\frac{\delta E_{xc}}{\delta \rho(\mathbf{x})} = v_{xc}(\mathbf{x}) \qquad \text{Exchange-correlation potential}$$

$$\frac{\delta \rho(\mathbf{x}')}{\delta \phi_k(\mathbf{x})} = \frac{\partial}{\partial \phi_k(\mathbf{x})} \sum_i^n |\phi_i(\mathbf{x}')|^2 = 2\phi_k(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')$$

$$\frac{\delta E_{xc}}{\delta \phi_k(\mathbf{x})} = 2 \int v_{xc}(\mathbf{x}')\phi_k(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}') \, d\mathbf{x}' = 2v_{xc}(\mathbf{x})\phi_k(\mathbf{x})$$

Kohn–Sham equations

Optimise the Kohn–Sham Lagrangian

$$L[\phi] = T_s[\phi] + V[\phi] + J[\phi] + E_{xc}[\phi] - \sum_{ij} \epsilon_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$

$$\frac{\delta L}{\delta \phi_k(\mathbf{x})} = 2 \left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \hat{J} \right) \phi_k(\mathbf{x}) + \frac{\delta E_{xc}}{\delta \phi_k(\mathbf{x})} - 2 \sum_{kj} \epsilon_{kj} \phi_j(\mathbf{x}) = 0$$

The Kohn–Sham equations are analogous to the Hartree–Fock equations

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \hat{J} + v_{xc}(\mathbf{x}) \right) \phi_k(\mathbf{x}) = \epsilon_k \phi_k(\mathbf{x})$$

- The ficticious non-interacting electrons experience an effective potential $v_{xc}(\mathbf{x})$ that ensures ρ is the exact ground state density
- Both $\hat{J}$ and v_{xc} depend on $\phi \Rightarrow$ self consistent solution
- In practice $E_{xc}[\rho]$ is not known and must be approximated

Numerical implementation

The KS orbitals are expanded using a LCAO with GTOs

$$\phi_k(\mathbf{x}) = \sum_u^m \chi_u(\mathbf{x}) C_{uk}$$

$$\sum_v^m \langle \chi_u | \hat{F}_{\mathrm{KS}} | \chi_v \rangle C_{vk} = \sum_v^m \langle \chi_u | \chi_v \rangle C_{vk} \epsilon_k$$

The KS Fock matrix is evaluated in the AO basis

$$\langle \chi_u | \hat{F}_{\mathrm{KS}} | \chi_v \rangle = \langle \chi_u | \, \hat{h}_1 \, | \chi_v \rangle + \langle \chi_u | \, \hat{J} \, | \chi_v \rangle + \langle \chi_u | v_{xc}(\mathbf{r}) | \chi_v \rangle$$

The only change from HF theory is that $v_{xc}(\mathbf{r})$ is a complicated function of the density. The integrals are evaluated by quadrature on tessalated atom-centred grids: grid points $\mathbf{r}_I$ and weights w_I

$$\langle \chi_u | \hat{v}_{ex}(\mathbf{r}) | \chi_v \rangle \approx \sum_I w_I \, \chi_u^*(\mathbf{r}_I) v_{ex}(\mathbf{r}_I) \chi_v(\mathbf{r}_I)$$

The exchange-correlation functional

The formal definition of $E_{xc}[\rho]$ is

$$E_{xc}[\rho] = F[\rho] - T_s[\rho] - J[\rho]$$

KS theory provides the two largest contributions to $F[\rho]$. The unkown $E_{xc}[\rho]$ is realtively small and can be decomposed further

$$\begin{aligned} E_x[\rho] &= \langle \Phi | \hat{K} | \Phi \rangle && \textit{exchange} \\ E_c[\rho] &= \langle \Psi | \hat{H} | \Psi \rangle - \langle \Phi | \hat{H} | \Phi \rangle && \textit{correlation} \end{aligned}$$

The correlation term further decomposes into potential and kinetic energies

$$\begin{aligned} E_c[\rho] &= \langle \Psi | \hat{T} | \Psi \rangle - \langle \Phi | \hat{T} | \Phi \rangle + \langle \Psi | \hat{V}_{ee} | \Psi \rangle - \langle \Phi | \hat{V}_{ee} | \Phi \rangle \\ &= T_c[\rho] + U_c[\rho] \end{aligned}$$

These decompositions have not proved useful. Approximations to $E_{xc}[\rho]$ work far better than using exact exchange $E_x[\rho]$ and approximating $E_c[\rho]$.

The uniform electron gas (jellium)

Insight into E_{xc} can be gained by studing simple models.

Place n electrons in a cubic box of volume V and impose periodic boundary conditions so that the density $\rho(\mathbf{r}) = n/V$ is uniform throughout the box. The UEG is the limit of an infinitely large box.

The orbitals are just the plane wave momentum states $\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{2\pi}} e^{i\mathbf{k}\cdot\mathbf{r}}$

Analytic expressions for $T_s[\rho]$ and $E_x[\rho]$ can be derived

$$T_s[\rho] = C_F \int \rho(\mathbf{r})^{5/3}\, d\mathbf{r}$$

$$E_x[\rho] = -C_x \int \rho(\mathbf{r})^{4/3}\, d\mathbf{r}$$

Accurate numerical simulation by Ceperley and Alder allowed Vosko, Wilk and Nusair (VWN) to obtain a good approximation of $E_c[\rho]$. Perdew and Wang obtained an improved functional PW91.

The local spin density approximation

In the local density approximation the functional takes the form

$$E_{xc}[\rho] = \sum_{\sigma} \int \rho_\sigma(\mathbf{r})\, \varepsilon_{xc}(\rho_\sigma(\mathbf{r}))\, d\mathbf{r}$$

Density of alpha and beta electrons $\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})$

$\varepsilon_{xc}(\rho(\mathbf{r}))$ is a local energy that depends on the density at that point.

$\varepsilon_{xc}(\rho(\mathbf{r}))$ is the local energy for the uniform electron gas

$$\varepsilon_{xc}(\rho(\mathbf{r})) = -C_x \rho(\mathbf{r})^{1/3} + \varepsilon_c^{UEG}(\rho(\mathbf{r}))$$

$\varepsilon_c^{UEG}(\rho(\mathbf{r}))$ is either $\varepsilon_c^{VWN}(\rho(\mathbf{r}))$ or $\varepsilon_c^{PW91}(\rho(\mathbf{r}))$

- Works well for metals
- Performs poorly for molecules where electrons are confined
  - Only 80% of E_x is recovered and E_c is 2 times too large

Scaling arguments

Constraints on possible forms of $E_x[\rho]$ can be deduced by examining the behaviour when scaling the coordinates $\lambda\mathbf{r}$

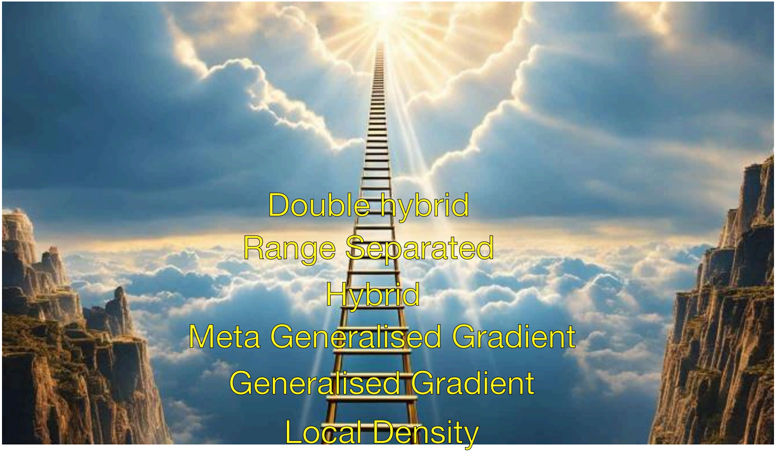
$$\phi_{k\lambda}(\mathbf{r}) = \lambda^{3/2}\phi_k(\lambda\mathbf{r}) \qquad \text{scaled orbitals}$$

$$\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r}) \qquad \text{scaled density}$$

Note that $\langle\phi_{k\lambda}|\phi_{k\lambda}\rangle = \int |\phi_k(\lambda\mathbf{r})|^2\lambda^3 d\mathbf{r} = \int |\phi_k(\mathbf{r}')|^2 d\mathbf{r}' = 1$

$$\begin{aligned} E_x[\Phi_\lambda] &= \frac{1}{2}\sum_{ij}^{n}\int\int \frac{\phi_i(\lambda\mathbf{r}_1)\phi_j(\lambda\mathbf{r}_2)\phi_j(\lambda\mathbf{r}_1)\phi_i(\lambda\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|}\,\lambda^3 d\mathbf{r}_1\lambda^3 d\mathbf{r}_2 \\ &= \lambda\frac{1}{2}\sum_{ij}^{n}\int\int \frac{\phi_i(\lambda\mathbf{r}_1)\phi_j(\lambda\mathbf{r}_2)\phi_j(\lambda\mathbf{r}_1)\phi_i(\lambda\mathbf{r}_2)}{|\lambda\mathbf{r}_2 - \lambda\mathbf{r}_1|}\,\lambda^3 d\mathbf{r}_1\lambda^3 d\mathbf{r}_2 \\ &= \lambda E_x[\Phi] \qquad \text{Therefore } E_x[\rho_\lambda] = \lambda E_x[\rho] \end{aligned}$$

Jacobs Ladder



Density Functional Approximations

- Local Density Approximation

$$E_{xc}^{\mathrm{LDA}}[\rho] = \sum_{\sigma} \int \rho_{\sigma}(\mathbf{r})\, \varepsilon_{xc}(\rho_{\sigma}(\mathbf{r}))\, d\mathbf{r}$$

- Generalised Gradient Approximation

dimensionless gradient

$$E_{xc}^{\mathrm{GGA}}[\rho] = \sum_{\sigma} \int \rho_{\sigma}\, \varepsilon_{xc}(\rho_{\sigma}, x_{\sigma})\, d\mathbf{r} \qquad x(\mathbf{r}) = \frac{|\nabla \rho(\mathbf{r})|}{\rho^{4/3}}$$

- Meta Generalised Gradient Approximation

kinetic energy density

$$E_{xc}^{\mathrm{mGGA}}[\rho] = \sum_{\sigma} \int \rho_{\sigma}\, \varepsilon_{xc}(\rho_{\sigma}, x_{\sigma}, \tau_{\sigma})\, d\mathbf{r} \qquad \tau(\mathbf{r}) = \frac{1}{2} \sum_{i} |\nabla \phi_i(\mathbf{r})|^2$$

Density Functional Approximations

- Hybrid functionals use some exact exchange

$$E_{xc}^{\mathrm{Hyb}}[\rho] = aE_x[\rho] + (1-a)E_x^{\mathrm{GGA}}[\rho] + E_c^{\mathrm{GGA}}[\rho]$$

- Range separated Hybrid functionals

$$E_{xc}^{\mathrm{LC}}[\rho] = E_x^{\mathrm{lr}}[\rho] + (1-a)E_x^{\mathrm{sr,GGA}}[\rho] + E_c^{\mathrm{GGA}}[\rho]$$

- Double Hybrid functionals

$$E_{xc}^{\mathrm{DH}}[\rho] = aE_x[\rho] + (1-a)E_x^{\mathrm{GGA}}[\rho] + bE_c^{\mathrm{MP2}} + (1-b)E_c^{\mathrm{GGA}}[\rho]$$

- Dispersion corrected functionals

$$E_{xc}^{\mathrm{DFT\text{-}D}}[\rho] = E_{xc}[\rho] - s\sum_{I<J} C_6(IJ)\frac{f(R_{IJ})}{R_{IJ}^6}$$

Generalised Gradient Approximation

The exchange energy of a slowly varying inhomogeneous electron gas is

$$E_x[\rho] = -C_x \int \rho(\mathbf{r})^{4/3}(1 + C_{x2}x^2(\mathbf{r}))\, d\mathbf{r} \qquad x(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})}$$

The dimensionless gradient $x(\mathbf{r})$ diverges in the orbital tails $\phi(\mathbf{r}) \sim e^{-\alpha r}$

Becke's exchange functional for molecules damps the divergence

$$E_x^{\mathrm{B88}}[\rho] = E_x^{\mathrm{LDA}}[\rho] + \sum_\sigma \int \rho_\sigma^{4/3} \frac{\gamma x_\sigma^2}{1 + 6\gamma \sinh^{-1}(x_\sigma)}\, d\mathbf{r}$$

Least squares fit to exact E_x for rare gas atoms (He-Kr) gave $\gamma = 0.0042$

Lee Yang and Parr constructed a correlation energy functional derived from an accurate correlated wavefunction for the helium atom

$$E_c^{\mathrm{LYP}}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}), x(\mathbf{r}))\, d\mathbf{r} \qquad \text{complicated } \varepsilon_{xc}$$

Generalised Gradient Approximation

Perdew Burke and Ernzerhof developed GGA functionals for both E_x and E_c that recover the UEG and slowly varying imhomogeneous electron gas limits, but behave sensibly for rapidly varying densities.

- The PBE functional is designed for materials
- The BLYP functional is fit to atomic data and designed for chemistry

Atomisation Energies (kcal/mol)

method	HF	LDA	BLYP
RMSD	86	36	8

H_2 CH_2 NH_2 OH H_2O HF CN HCN CH_3NH_2 CO HCO H_2CO CH_3OH N_2 N_2H_4 NO HNO CF HCF CH_3F O_2 HO_2 H_2O_2 H_2S HCl HOF F_2 CS CO_2 SN CCl SO O_3 CH_3Cl SF ClO HOCl OCS S_2 SO_2 SCl ClO_2 Cl_2 CS_2

Bond lengths (Å)

molecule	bond	LDA	BLYP	expt
H_2	H−H	0.765	0.748	0.741
C_2H_6	C−C	1.510	1.542	1.526
	C−H	1.101	1.100	1.088
C_2H_4	C=C	1.327	1.339	1.339
	C−H	1.094	1.092	1.085
C_2H_2	C≡C	1.203	1.209	1.203
	C−H	1.073	1.068	1.061
RMSD		0.020	0.009	—

Self interaction error

Consider a one-electron example H_2^+ Hartree–Fock is exact

The correct behaviour is $E_x[\rho] = -J[\rho]$ exchange cancels self repulsion

At $R_{AB} \to \infty$ the density is $\rho(\mathbf{r}) = \frac{1}{2}\rho_A(\mathbf{r}) + \frac{1}{2}\rho_B(\mathbf{r})$ $\rho_A = \rho_B = \phi_{1s}^2$

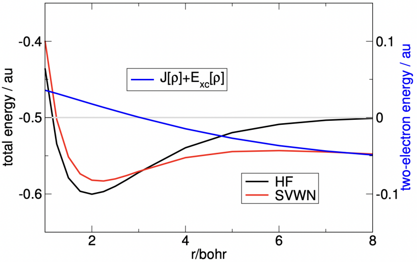
$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \tfrac{1}{4}\left(J[\rho_A] + J[\rho_B]\right)$$

$$E_x^{\mathrm{LDA}} = \int \rho^{4/3}(\mathbf{r})\, d\mathbf{r}$$

$$= 2^{-4/3}\left(E_x^{\mathrm{LDA}}[\rho_A] + E_x^{\mathrm{LDA}}[\rho_B]\right)$$

$$\approx -0.6\left(J[\rho_A] + J[\rho_B]\right)$$



- LDA and GGA functionals have a large SIE (aka delocalisation errors)
  - Too low reaction barriers; overbinding of charge transfer complexes

Hybrid Functionals

In 1993 Becke proposed to mix exact exchange with the BLYP functional

$$E_{xc}^{\mathrm{B3LYP}}[\rho] = aE_x[\rho] + bE_x^{\mathrm{B88}}[\rho] + (1-a-b)E_x^{\mathrm{LDA}}[\rho] \\ + cE_c^{\mathrm{LYP}}[\rho] + (1-c)E_c^{\mathrm{VWN}}[\rho]$$

Fit to energies of small atoms and molecules $a = 0.20$ $b = 0.72$ $c = 0.81$

The PBE hybrid is $E_{xc}^{\mathrm{PBE0}}[\rho] = 0.25E_x[\rho] + 0.75E_x^{\mathrm{PBE}}[\rho] + E_c^{\mathrm{PBE}}[\rho]$

Mean absolute errors		HF	BLYP	B3LYP
$r_e/\text{Å}$:	12 first row diatomics	0.024	0.012	0.004
$r_e/\text{Å}$:	12 second row diatomics	0.016	0.024	0.006
v_0/cm^{-1}:	122 molecules	50	45	34
$D_0/\mathrm{kcal\ mol}^{-1}$:	44 molecules	86	8	5
$\Delta E^\dagger/\mathrm{kcal\ mol}^{-1}$	Diels-Alder forward	24	-1	1
$\Delta E^\dagger/\mathrm{kcal\ mol}^{-1}$	Diels-Alder reverse	-8	-16	-9

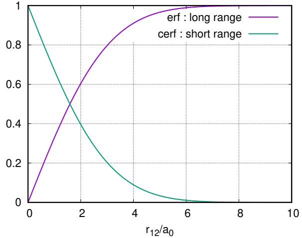
- B3LYP accurate enough to interpret and rationalise structure, thermodynamics, mechanism and molecular spectra

Range separation

Exchange can be partitioned into long- and short-range contributions

$$\frac{1}{r_{12}} = \frac{\mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\mathrm{cerf}(\mu r_{12})}{r_{12}}$$

$$E_x = E_x^{lr} + E_x^{sr} \qquad \mu = 0.33$$



By using a higher proportion of exact exchange at long range, the exchange correlation potential is closer to the asymptotic form of $v_{xc}(r) = -\frac{1}{r} + C$

- Important for polarisibilities and charge-transfer processes

$$E_{xc}^{\text{CAM-B3LYP}} = aE_x^{sr} + bE_x^{lr} + (1-a)E_x^{sr,\text{B88}} + (1-b)E_x^{lr,\text{B88}} + E_c^{\text{LYP}}$$

Parameters fit to atomisation energies and ionisation potentials

Short range: 20% E_x, 80% E_x^{B88}

Long range: 60% E_x, 40% E_x^{B88}

Dispersion

Dispersion is completely absent in local density correlation functionals

- Dispersion is correlation between electrons in separated densities

Important when modelling large systems or non-covalent interactions

Either

- Add empirical atom-atom dispersion correction damped at short R_{IJ}

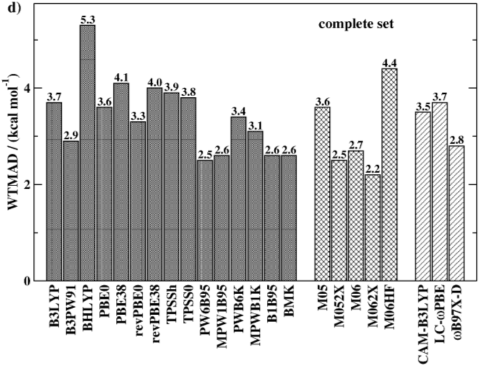
$$E_{xc}^{\text{DFT-D}}[\rho] = E_{xc}[\rho] - s \sum_{I<J} C_6(IJ) \frac{f(R_{IJ})}{R_{IJ}^6}$$

- Add an *a postiori* MP2 correlation energy correction using KS energies

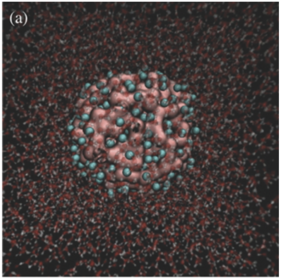
$$E_{xc}^{\text{B2PLYP}}[\rho] = aE_x[\rho] + (1-a)E_x^{\text{B88}}[\rho] + bE_c^{\text{MP2}} + (1-b)E_c^{\text{LYP}}[\rho]$$

$a = 0.53$ $b = 0.27$

State of the art



Overall accuracy has not improved much over time (still 2-3 kcal/mol)



Very large-scale calculations possible: H_2 formation on metal nano-particle

$n = 50000, m = 100000$ and 1000 time steps