If we ignore the exclusion principle, then the 2-electron Schrödinger equation can be reduced to 2 equations

$$\left[\frac{1}{2}\nabla_a^2 + E_a - V_a(r_a)\right]\psi_a(r_a) = 0 \qquad \{a = 1, 2\}$$

In the non-interacting electrons approximation $V_a(r_a) = -Z/r_a$, but we can improve on this by following Hartree's method which suggests that $V_a(r_a)$ can be taken to be the potential seen by electron a due to the combined field of the nucleus and electron b. To obtain $V_1(r_1)$ for instance, we set the equation

$$V_1(r_1) = -\frac{Z}{r_1} + \int \frac{1}{r_{12}} |\psi_2(r_2)|^2 \, d\tau_2$$

- $V_1(r_1)$: effect. potential seen by elec 1.
- $-\frac{Z}{r_1}$: nuclear field
- $\frac{1}{r_{12}}$: 2nd electron field
- $|\psi_2(r_2)|^2$: probability of electron 2 being at r_2

similarly $2 \leftrightarrow 1$, giving 2 simultaneous equations.

The binding energy of the system is

$$E = E_1 + E_2 - \iint |\psi_1(r_1)|^2 \frac{1}{r_{12}} |\psi_2(r_2)|^2 \, d\tau_1 \, d\tau_2$$

↑ Subtracted since it has been included twice, once in V_1 (or E_1) and in V_2 (or E_2)

Equations for $V_1(r_1)$ and $V_2(r_2)$ are to be solved iteratively, starting from some guess / trial function.

Hartree's Self consistent Field method does not take into account the Pauli exclusion principle.

The generalisation of the Hartree-SCF method was done by Fok, who proposed that if $\Psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_n)$ is a suitably antisymmetrised grand wavefunction which is composed of linear combinations of products of spin-orbital wavefunctions, ϕ_i (e.g. Slater determinant) then the grand wavefunction Ψ must be such that it corresponds to the minimum of the Energy w.r.t. variations in the spin orbitals ϕ_i subject to the constraint

That is

$$\frac{\delta}{\delta \phi_i}\left[\langle \hat{H} \rangle - E \sum_j \int |\phi_j|^2 \, d\tau_j \right] = 0$$

$\langle \hat{H} \rangle$: full hamiltonian; $\int |\phi_j|^2 \, d\tau_j$: normalisation constraint

$$\langle \Psi | \hat{H} | \Psi \rangle = \text{minimum} \qquad \langle \Psi | \Psi \rangle = 1.$$

$$\iint \delta\Psi^* (\hat{H} - E) \Psi \, d\tau_1 \, d\tau_2 = 0 \qquad \{\text{constrained extremum}\}$$

$$\left[\frac{1}{2}\nabla^2 + \frac{Z}{r} + E - H_{22} - G_{22}(r) \right] \phi_1(r) + \left[H_{12} + G_{12}(r) \right] \phi_2(r) = 0$$

$$\left[\frac{1}{2}\nabla^2 + \frac{Z}{r} + E - H_{11} - G_{11}(r) \right] \phi_2(r) + \left[H_{12} + G_{12}(r) \right] \phi_1(r) = 0$$

where $G_{ab}(r_1) = \int \phi_a(r_2) \, \phi_b(r_2) \, \frac{1}{r_{12}} \, d\tau_2$

[similarly $G_{ab}(r_2)$]

$$H_{ab} = \int \phi_a \left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} \right] \phi_b \, d\tau$$

$[a, b = 1, 2]$

These two equations are to be solved simultaneously.

The generalised form of the antisymmetrised many particle wavefunct. composed of one-particle spin-orbitals is given by the Slater determnt.

$$\Psi(\vec{r}_1 \cdots \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \cdots & \phi_n(1) \\ \phi_a(2) & & & \\ \vdots & & & \\ \phi_a(N) & & & \phi_n(N) \end{vmatrix}$$

The spin-orbitals are orthonormalised, i.e. $\langle \phi_a | \phi_b \rangle = \delta_{\alpha\beta}$
Since the spin variables only take values $\pm\frac{1}{2}$, it follows that the space orbitals corresponding to the same spin function be orthonormal.

The slater det. is sometimes written in the form

$$\Psi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \, \phi_a(1) \cdots \phi_n(N) \equiv \sqrt{N!}\, \mathcal{A} \Phi_\Psi$$

where $A = \frac{1}{N!} \sum (-)^P P$

The direct product $\psi^{(H)} = \phi_a(1) \cdots \phi_n(N)$ is called the Hartree wavefn.

The Hamiltonian of the N-particle system is

$$\hat{H} = \underbrace{-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}}_{H_{NI}\ \text{(non-interacting)}} + \underbrace{\sum_{i>j} \frac{1}{r_{ij}}}_{H_I\ \text{(interacting)}} \qquad \left\{ \hat{H}_{NI} = \sum_i \hat{h}_i \right\}$$

The energy of this system ~~$E[\Psi]$~~ $E[\Psi]$ is $\langle \Psi | \hat{H} | \Psi \rangle$

$$\langle \Psi | \hat{H} | \Psi \rangle = \left\langle \Psi \middle| \sum_i \hat{h}_i + \sum_{i>j} \frac{1}{r_{ij}} \middle| \Psi \right\rangle$$

We note that $\frac{1}{\sqrt{N!}} (-1)^P P \frac{1}{\sqrt{N!}} (-1)^P P \Phi_\Psi \neq \frac{1}{\sqrt{N!}} (-1)^P P \Psi$

$\langle \Psi | \sum \hat{h}_i | \Psi \rangle = \sum_i \langle \phi_i | h_i | \phi_i \rangle$

$\langle \Psi | \hat{H}_{int} | \Psi \rangle$ ✗

2-electron Hartree-Fock equations

$$\left[-h_1 + E - H_{22} - G_{22}(r_1)\right]\phi_1(r_1) + \left[H_{12} + G_{12}(r_1)\right]\phi_2(r_1) = 0$$

$$\left[-h_2 + E - H_{11} - G_{11}(r_2)\right]\phi_2(2) + \left[H_{12} + G_{12}(r_2)\right]\phi_1(r_2) = 0$$

where $\hat{h}_{1,2} = -\frac{1}{2}\nabla^2_{1,2} - \frac{Z}{r_{1,2}}$; generically written simply as $\hat{h}$

and.

$$H_{ij} = \int \psi_1 \hat{h} \psi_2 \, d\tau$$

$$G_{ij}(\vec{r}_1) = \int \psi_i(\vec{r}_1)\, \psi_j(\vec{r}_2)\, \frac{1}{r_{12}}\, d\tau_2$$

$$G_{ij}(\vec{r}_2) = \int \psi_i(\vec{r}_1)\, \psi_j(\vec{r}_2)\, \frac{1}{r_{12}}\, d\tau_1$$

$$E = \langle \Psi | \hat{H} | \Psi \rangle \; ; \quad \Psi = \psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)$$

Generalisation to many electrons ($a = 1, \ldots n$)

$$h_i \phi_a(\vec{r}_i) + \left[\sum_b \int \phi_b^*(\vec{r}_j)\, \frac{1}{r_{ij}}\, \phi_b(\vec{r}_j)\, d\tau_j\right]\phi_a(\vec{r}_i)$$

$$- \sum_b \left[\int \phi_b(r_j)\, \frac{1}{r_{ij}}\, \phi_a(r_j)\, d\tau_j\right]\phi_b(\vec{r}_i) = E_a \phi_a(\vec{r}_i)$$

$$\langle E \rangle = \sum_a I_a + \frac{1}{2}\sum_a \sum_b (J_{ab} - K_{ab})$$

$$I_a = \int \phi_a^*\, h\, \phi_a \, d\tau$$

$$J_{ab} = \int |\phi_a(r_i)|^2\, \frac{1}{r_{ij}}\, |\phi(r_b)|^2 \, d\tau_i \, d\tau_j$$

$$K_{ab} = \int \phi_a^*(r_j)\, \phi_b^*(r_i)\, \frac{1}{r_{ij}}\, \phi_a(r_i)\, \phi_b(r_j)$$

$$= \int \phi_a^*(r_j)\, \phi_a(r_i)\, \frac{1}{r_{ij}}\, \phi_b^*(r_i)\, \phi_a(r_j)$$

A collection of atoms has atoms in superpositions of their eigenstates. They make transitions between eigenstates under the action of an external perturbation.

Without loss of generality, we may model this system by a two-level system between which transitions occur under an external influence.

The perturbation is a time dependent perturbation $\hat{H}'$ to the original hamiltonian $\hat{H}_0$ and the equation of motion of this system is

originally: $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi$

with solutions $\Psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$

to which we apply the shorthand: $\omega_n = E_n/\hbar$, so that

$$\Psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{-i\omega_n t}$$

and the general state of the system (unperturbed) would be

$$\Psi \equiv \Psi_{(grand)} = \sum_n \psi_n(\vec{r})\, e^{-i\omega_n t}$$

For a two level atom this reduces to $\Psi = c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}$ with $|c_1|^2 + |c_2|^2 = 1$, to conserve probability.

To find the changes due to the perturbation we need to solve

$$i\hbar \frac{\partial \Psi}{\partial t} = (\hat{H}_0 + \hat{H}')\Psi$$

substituting $\Psi = c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}$ in the above, we get

$$i\hbar\left[-i\omega_1 c_1 \psi e^{-i\omega_1 t} + \dot{c}_1\psi_1 e^{-i\omega_1 t} - i\omega_2 c_2 e^{-i\omega_2 t} + \dot{c}_2\psi_2 e^{-i\omega_2 t}\right]$$
$$= \hat{H}_0\left[c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}\right] + \hat{H}'\left[c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}\right]$$

$$i\hbar\left[\dot{c}_1 e^{-i\omega_1 t}\psi_1 + \dot{c}_2 e^{-i\omega_2 t}\psi_2\right] = \hat{H}'\left[c_1 e^{-i\omega_1 t}\psi_1 + c_2 e^{-i\omega_2 t}\psi_2\right]$$

we premultiply the eqn by ψ_1^* or ψ_2^* and perform a spatial integration

$$i\hbar\left[\dot{c}_1 e^{-i\omega_1 t}\langle\psi_1|\psi_1\rangle + \dot{c}_2 e^{i\omega_2 t}\langle\psi_1|\psi_2\rangle\right] = c_1 e^{-i\omega_1 t}\langle\psi_1|\hat{H}'|\psi_1\rangle + c_2 e^{-i\omega_2 t}\langle\psi_1|\hat{H}'|\psi_2\rangle$$

$\langle\psi_1|\psi_1\rangle = 1$, $\langle\psi_1|\psi_2\rangle = 0$, $\langle\psi_1|\hat{H}'|\psi_1\rangle = H'_{11}$, $\langle\psi_1|\hat{H}'|\psi_2\rangle = H'_{21}$

$$i\hbar\, \dot{c}_1\, e^{-i\omega_1 t} = c_1 e^{-i\omega_1 t} H'_{11} + c_2 e^{-i\omega_2 t} H'_{21}$$

$$\therefore \quad \dot{c}_1 = \frac{-i}{\hbar}\left[c_1 H'_{11} + c_2 H'_{21} \exp\left[-i(\omega_2-\omega_1)t\right]\right]$$

- $\dot{c}_1$: rate of change of population of ψ_1
- H'_{11}, H'_{21}: matrix elements of the perturbation
- $\omega_2-\omega_1$: resonance condition for mixing ψ_1 and ψ_2

Had we pre-multiplied by ψ_2^* we would have got the condition for c_2

$$\dot{c}_2 = \frac{-i}{\hbar}\left[c_1 H'_{21} \exp\left[+i(\omega_2-\omega_1)t\right] + c_2 H'_{22}\right]$$

we use the shorthand: $\omega_{21} = \omega_2 - \omega_1$ henceforth

EXTERNAL RADIATION AS A PERTURBATION

In this case the perturbing field is an oscillating electric and magnetic fields that are out of phase

$$\mathcal{E} = \mathcal{E}_0 \exp\left[i(Kx-\omega t)\right]$$
$$\mathcal{B} = \mathcal{B}_0 \exp\left[i(Kx-\omega t+\pi/2)\right]$$

Since the typical wavelengths λ associated with visible or UV radiation (which is energetic enough to excite most atoms) is much larger than the atomic size, [$\lambda \cong 100\,nm$, $r_{atom} \sim 0.1\,nm$], we may take the electric field to be constant in space for this treatment of radiation interaction.

constant in space $\Rightarrow$ $e^{iKx} = 1 + iKx + (iKx)^2/2! + \cdots \simeq 1$

Thus we can take $\mathcal{E} = \mathcal{E}_0 \cos(\omega t)$ and $\mathcal{B} = \mathcal{B}_0 \sin(\omega t)$.
The magnetic interaction with radiation is $-\vec{\mu}\cdot\vec{\mathcal{B}}$
The electric interaction with radiation is $-\vec{p}\cdot\vec{\mathcal{E}}$
The former is much weaker than the latter and is hence ignored.

Thus $\hat{H}' = -\vec{p}\cdot\vec{\mathcal{E}}$

$= +ez\,\mathcal{E}_0\cos(\omega t)$

since $\vec{p} = -e\vec{r}$ and $\hat{\mathcal{E}}_0$ may be taken to be along $\hat{z}$

CALLED DIPOLE APPROXIMATION

We then obtain

$$H'_{11} = \langle \psi_1 | z | \psi_1 \rangle \mathcal{E}_0 \cos(\omega t) \Big\} \equiv 0$$
$$H'_{22} = \langle \psi_2 | z | \psi_2 \rangle \mathcal{E}_0 \cos(\omega t)$$

These two matrix elements are identically zero due to the odd parity of z but

$H'_{21} = H'_{12} = \langle \psi_1 | z | \psi_2 \rangle \mathcal{E}_0 \cos(\omega t)$ can be non-zero, if ψ_1 and ψ_2 are of opposite parities.

If we define $\Omega_{21} = \frac{e\mathcal{E}_0}{\hbar} \langle \psi_1 | z | \psi_2 \rangle$, then the equations for $\dot{c}_1$ and $\dot{c}_2$ take the form

$$\dot{c}_1 = -i\Omega_{21} \cos(\omega t)\, e^{-i\omega_{21}t}\, c_2$$

$$\dot{c}_2 = -i\Omega_{21} \cos(\omega t)\, e^{+i\omega_{21}t}\, c_1$$

- Ω is called "Rabi Frequency"
- Ω_{21} is interpreted as the "hopping" rate between states 1 and 2
- Ω_{21} is not to be confused with the freq of radiation, which is ω_{21}

The quantity $e\langle \psi_2 | z | \psi_1 \rangle$ is the expectation value of the quantum mechanical dipole moment, called the dipole matrix element

WEAK RADIATION

Let us assume that the external radiation is weak, i.e. $N_{photons} \ll N_{atoms}$
If the atoms are originally in their ground state (usually the case, since temperatures are low compared to excitation energies), then we can make a further approximation:

$$c_2(t) \ll c_1(t) \quad \forall t \; ; \quad c_1(t) \simeq 1$$

but $c_2(t) \neq 0$ and $|c_1(t)|^2 + |c_2(t)|^2 = 1$ at all times.

The earlier equations simplify to

$$\dot{c}_2 = -i\Omega_{21} \cos(\omega t')\, e^{+i\omega_{21}t'}$$ [where t' is the running variable for time]

$$= \frac{-i}{2}\Omega_{21} \left\{ \exp\left[i(\omega+\omega_{21})t'\right] + \exp\left[-i(\omega-\omega_{21})t'\right] \right\}$$

~~edited~~ *

To obtain $c_2(t)$ from this equation we need to integrate from $t'=0$ to $t'=t$. Noting that $c_2(0)=0$, we get

$$c_2(t) = -\frac{1}{2}\Omega_{21}\left[\frac{e^{i(\omega+\omega_{21})t'}}{\omega+\omega_{21}} - \frac{e^{-i(\omega-\omega_{21})t'}}{\omega-\omega_{21}}\right]_0^t$$

$$= \frac{1}{2}\Omega_{21}\left[\frac{1-e^{i(\omega+\omega_{21})t}}{\omega+\omega_{21}} - \frac{1-e^{-i(\omega-\omega_{21})t}}{\omega-\omega_{21}}\right]$$

If ω and ω_{21} differ widely, then $|c_2(t)|^2$ changes very slowly and the system mostly stays in $|1\rangle$ with weak oscillations to $|2\rangle$.

However, if $\omega \simeq \omega_{21}$ then the second term makes a large contribution to $c_2(t)$ and we may write

$$c_2(t) = -\frac{1}{2}\Omega_{21}\left[\frac{1-e^{-i(\omega-\omega_{21})t}}{(\omega-\omega_{21})}\right]$$

$$= -\frac{1}{2}\Omega_{21}\, e^{-i(\omega-\omega_{21})t/2}\left[\frac{e^{+i(\omega-\omega_{21})t/2} - e^{-i(\omega-\omega_{21})t/2}}{\omega-\omega_{21}}\right]$$

$$\therefore \left[|c_2(t)|^2 = \left(\frac{\Omega_{21}}{2}\right)^2 \left[\frac{\sin[(\omega-\omega_{21})t/2]}{(\omega-\omega_{21})/2}\right]^2\right]$$

This is the probability of transition to state $|2\rangle$ from state $|1\rangle$. Recall, that $\Omega_{21} = eE_0\langle z_{21}\rangle/\hbar$, so under this approximation only states with different parities are coupled.