Strategies for the Many-Body Problem

- Start with **Independent Particle model**, e.g. Hartree-Fock ("the best" Independent Particle model)
- Define a zeroth order configuration (a "vacuum level")
- Expand beyond this stepwise

Simple Perturbation approach for 2 particles

- Basic idea

$$H = H_0 + V$$

- H_0 is simple

$$H_0 = \sum_i h_i$$

- and solved

$$H_0\Psi_0 = E_0\Psi_0 = \left(\sum_i \epsilon_i\right)\Psi_0$$

Simple Example he-like system

$$H = \sum_{i=1,2}\left(\frac{\hbar^2}{2m}\left(-\frac{\partial^2}{\partial r_i^2} + \frac{\ell_i(\ell_i+1)}{r_i^2}\right) - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_i}\right) + \frac{1}{r_{12}} = \sum_{i=1,2} h_i + \frac{1}{r_{12}}$$

$$\begin{aligned}\Psi &= \Psi_0 + \delta\Psi \\ \Psi_0 &= \mid \{ab\}\rangle = \frac{\mid ab\rangle - \mid ba\rangle}{\sqrt{2}}\end{aligned}$$

Simple Perturbation approach for 2 particles

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$$\begin{aligned} H\Psi &= E\Psi \\ (H_0 + V)(\Psi_0 + \delta\Psi) &= (E_0 + \delta E)(\Psi_0 + \delta\Psi) \\ (E_0 - H_0)\,\delta\Psi &= V(\Psi_0 + \delta\Psi) - \delta E(\Psi_0 + \delta\Psi) \end{aligned}$$

- intermediate normalization
- integrate with Ψ_0 from the left

$$\langle \Psi_0 \mid \Psi_0 \rangle = 1,\ \langle \Psi_0 \mid \delta\Psi \rangle = 0$$

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Simple Perturbation approach for 2 particles

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$$
\begin{aligned}
(E_0 - H_0)\,\delta\Psi = \ & V(\{ab\} + \delta\Psi) - \mid \{ab\}\rangle\langle\{ab\} \mid V \mid \{ab\} + \delta\Psi\rangle - \\
& \delta E \delta\Psi
\end{aligned}
$$

Simple Perturbation approach for 2 particles

$$\sum_{rs} \mid \{rs\}\rangle\langle\{rs\} \mid = 1$$

$$\begin{aligned}
(\epsilon_a + \epsilon_b - h_1 - h_2)\,\delta\Psi^i = & \sum_{\{rs\}\neq\{ab\}} \mid \{rs\}\rangle\langle\{rs\} \mid \frac{1}{r_{12}} \mid \{ab\} + \delta\Psi^{i-1}\rangle \\
-\delta E \delta\Psi^{i-1} & \\
\delta E = & \langle ab \mid \frac{1}{r_{12}} \mid ab\rangle - \langle ba \mid \frac{1}{r_{12}} \mid ab\rangle + \ldots \\
\delta\Psi^{(1)} = & \sum_{\{rs\}\neq\{ab\}} \frac{\mid \{rs\}\rangle\langle\{rs\} \mid \frac{1}{r_{12}} \mid \{ab\}\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}
\end{aligned}$$

- possible to solve iteratively
- slightly more to consider with $N > 2$ (but the idea is the same
- Economical since only one (or a few) states are solved for

Perturbation theory: HF starting-point

- with Hartree-Fock starting point $V = \frac{1}{r_{12}} - u_{hf}$
- small enough V required! Convergence not guaranteed.

$$\Psi_0 = \mid \alpha\rangle$$

$$\mid \alpha\rangle = \mid \{abc\ldots\}\rangle, \quad E_0 = \epsilon_a + \epsilon_b + \epsilon_c + \ldots$$

$$\delta\Psi^{(1)} = \sum_{\beta\neq\alpha} \frac{\mid \beta\rangle\langle\beta \mid V \mid \alpha\rangle}{E_0 - E_0^{\beta}}$$

$$V = \sum_{i<j}^{N} \frac{1}{r_{12}} - \sum_{i} u_{hf}\left(r_i\right)$$

- One one-particle perturbation and one two-particle perturbation!

Lowest order correction to the wf

- the contribution from u_{hf}

$$\delta\Psi_u^{(1)} = -\sum_{\beta\neq\alpha} \frac{|\,\beta\rangle\langle\beta\,|\sum_i u_{hf}(r_i)\,|\,\alpha\rangle}{E_0 - E_0^\beta}$$

- β must be a single excitation from α: $\beta = \alpha_a^r$

$$\begin{aligned}
\delta\Psi_u^{(1)} &= -\sum_{ar} \frac{|\,\alpha_a^r\rangle\langle\alpha_a^r\,|\sum_i u_{hf}(r_i)\,|\,\alpha\rangle}{\epsilon_a - \epsilon_r} \\
&= -\sum_{ar} \frac{|\,\alpha_a^r\rangle\langle r\,|\,u_{hf}\,|\,a\rangle}{\epsilon_a - \epsilon_r} \\
&= -\sum_{ar}\sum_b \frac{|\,\alpha_a^r\rangle\langle\{rb\}\,|\,\frac{1}{r_{12}}\,|\,\{ab\}\rangle}{\epsilon_a - \epsilon_r}
\end{aligned}$$

Lowest order correction to the wf

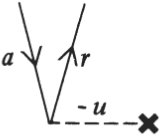
- the contribution from $1/r_{ij}$

$$\delta\Psi_C^{(1)} = \sum_{\beta\neq\alpha} \frac{\mid \beta\rangle\langle\beta \mid \sum_{i<j}\frac{1}{r_{ij}} \mid \alpha\rangle}{E_0 - E_0^\beta}$$

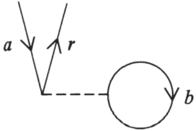
- β can be single OR a double excitations from α

$$\begin{aligned}\delta\Psi_C^{(1)} = & \frac{\mid \alpha_a^r\rangle\langle\alpha_a^r \mid \sum_{i<j}\frac{1}{r_{ij}} \mid \alpha\rangle}{\epsilon_a - \epsilon_r} + \sum_{abrs} \frac{\mid \alpha_{ab}^{rs}\rangle\langle\alpha_{ab}^{rs} \mid \sum_{i<j}\frac{1}{r_{ij}} \mid \alpha\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \\ = & \sum_{ar}\sum_{b} \frac{\mid \alpha_a^r\rangle\langle\{rb\} \mid \frac{1}{r_{12}} \mid \{ab\}\rangle}{\epsilon_a - \epsilon_r} + \frac{1}{2}\sum_{abrs} \frac{\mid \alpha_{ab}^{rs}\rangle\langle\{rs\} \mid \frac{1}{r_{12}} \mid \{ab\}\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}\end{aligned}$$

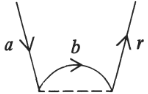
THE DIAGRAMS



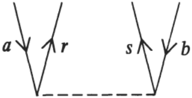
$$= \frac{|\alpha_a^r\rangle\langle r|-u|a\rangle}{\varepsilon_a - \varepsilon_r}$$



$$= \frac{|\alpha_a^r\rangle\langle rb|r_{12}^{-1}|ab\rangle}{\varepsilon_a - \varepsilon_r}$$



$$= -\frac{|\alpha_a^r\rangle\langle br|r_{12}^{-1}|ab\rangle}{\varepsilon_a - \varepsilon_r}$$



$$= \frac{1}{2}\frac{|\alpha_{ab}^{rs}\rangle\langle rs|r_{12}^{-1}|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}.$$

- Goldstone diagrams

Lowest order correction to the wf

- when starting from Hartree-Fock there are no single excitation corrections in first order!

$$\delta\Psi_C^{(1)} + \delta\Psi_{u_{hf}}^{(1)} = \qquad \frac{1}{2}\sum_{abrs} \frac{| \alpha_{ab}^{rs}\rangle\langle\{rs\} \mid \frac{1}{r_{12}} \mid \{ab\}\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

$$\delta E^{(2)} = \frac{1}{2}\sum_{abrs} \frac{\langle\{ab\} \mid \frac{1}{r_{12}} \mid \{rs\}\rangle\langle\{rs\} \mid \frac{1}{r_{12}} \mid \{ab\}\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

- (second order) correlation energy or
- Møller-Plesset perturbation theory in Quantum Chemistry
- will always lower the energy
- how does it scale?

Remember from last time:

$$\langle \alpha \mid H \mid \alpha \rangle = E_0 + \delta E^{(1)}$$
$$= \langle \alpha \mid \sum_i^N h_{HF}(i) + \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} - \sum_i^N u_{HF}(i) \mid \alpha \rangle$$
$$= \sum_a^{occ} \epsilon_a - \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \sum_{ab}^{occ} \langle ab \mid \frac{1}{r_{12}} \mid ab \rangle - \langle ba \mid \frac{1}{r_{12}} \mid ab \rangle \right)$$

Example Beryllium $1s^2 2s^2$ a.u.

E_{HF}	$-14.573\,023$
$\delta E^{(2)}$	$-0.076\,358$
h.o.	$-0.017\,309$

The perturbed wave function concept

- whenever there is a perturbation we can construct the perturbed wave functions caused by it
- also when the perturbation is time-dependent

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

if H is time-independent

$$\Psi\left(t,\mathbf{r}\right) = \Psi\left(0,\mathbf{r}\right)e^{-iEt/\hbar},\ \text{if } H\Psi\left(0,\mathbf{r}\right) = E\Psi\left(0,\mathbf{r}\right)$$

- with a time-dependent perturbation (for example $\mathbf{r}\cdot\mathbf{E}$, with $\mathbf{E} = 2E_z\cos\left(\omega t\right)\hat{z}$)

$$V\left(\mathbf{r},t\right) = 2z\cos\left(\omega t\right)E_z = z\left(e^{i\omega t} + e^{-i\omega t}\right)E_z$$

The perturbed wave function concept

- the solution $\mid a\rangle$ to h_{hf}

$$\psi_a(t) = \mid a\rangle e^{-i\epsilon_a t/\hbar}$$

- With the time dependent perturbation added

$$h = h_{hf} + z\left(e^{i\omega t} + e^{-i\omega t}\right)E_z$$

- There is a new time-dependent equation

$$\left(i\hbar\frac{\partial}{\partial t} - h_{hf}\right)\left(\psi_a(t) + \delta\psi_a(t)\right)$$
$$= zE_z\left(e^{i\omega t} + e^{-i\omega t}\right)\left(\psi_a(t) + \delta\psi_a(t)\right)$$

  - keep just the lowest order
  - divide up in $\pm$

$$\left(i\hbar\frac{\partial}{\partial t} - h_{hf}\right)\delta\psi_a^{\pm}(t) = zE_z\left(e^{\mp i\omega t}\right)\psi_a(t) = zE_z \mid a\rangle e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar}$$

  - starting from $\alpha = \{abc\ldots\}$ we can couple to $\alpha_a^r = \{rbc\ldots\}$

- what about the time dependence of $\delta\psi_a^{\pm}$?
- we expect it to oscillate with $exp\left(-i\left(\epsilon_a \pm \hbar\omega\right)t/\hbar\right)$

$$\delta\psi_a^{\pm} = \rho_a^{\pm}(r)e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar}$$

$$\begin{aligned}
\left(i\hbar\frac{\partial}{\partial t} - h_{hf}\right)\rho_a^{\pm}e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar} &= \quad \mid r\rangle\langle r \mid zE_z \mid a\rangle e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar} \\
\left(\epsilon_a \pm \hbar\omega - h_{hf}\right)\rho_a^{\pm} &= \quad \mid r\rangle\langle r \mid z \mid a\rangle E_z
\end{aligned}$$

- time-independent equation with solution

$$\rho_a^{\pm} = \sum_r \frac{\mid r\rangle\langle r \mid z \mid a\rangle}{\epsilon_a \pm \hbar\omega - \epsilon_r}E_z$$

- if the denominator strictly $\neq 0$ localized correction

RPAE

- The photon field interacts with all the electrons
- they all get a slight perturbation
- then the interaction between them changes!
- how can we account for that?

$$\langle r \mid u_{HF} \mid a \rangle = \sum_{b}^{occupied} = \langle \{rb\} \mid \frac{1}{r_{12}} \mid \{ab\} \rangle$$
$$\rightarrow \langle r \mid u_{HF} \mid a \rangle + \langle r \mid \delta u_{HF}^{\pm} \mid a \rangle$$

$$\langle r \mid \delta u_{HF}^{\pm} \mid a \rangle = \sum_{b}^{occupied} \langle \{rb\} \mid \frac{1}{r_{12}} \mid \{a\rho_b^{\pm}\} \rangle + \langle \{r\rho_b^{\mp}\} \mid \frac{1}{r_{12}} \mid \{ab\} \rangle$$

RPAE - Time Dependent HF

$$\langle r \mid \delta u_{HF}^{\pm} \mid a\rangle = \sum_{b}^{occupied} \langle\{rb\} \mid \frac{1}{r_{12}} \mid \left\{a\rho_b^{\pm}\right\}\rangle + \langle\left\{r\rho_b^{\mp}\right\} \mid \frac{1}{r_{12}} \mid \{ab\}\rangle$$

$$= \sum_{b}^{occ.} \sum_{rs}^{unocc.} \frac{\langle\{rb\} \mid \frac{1}{r_{12}} \mid \{as\}\rangle}{\epsilon_a \pm \hbar\omega - \epsilon_r} \frac{\langle s \mid z \mid b\rangle}{\epsilon_b \pm \hbar\omega - \epsilon_s}$$

$$+ \sum_{b}^{occ.} \sum_{rs}^{unocc.} \frac{\langle b \mid z \mid s\rangle}{\epsilon_b \mp \hbar\omega - \epsilon_s} \frac{\langle\{rs\} \mid \frac{1}{r_{12}} \mid \{ab\}\rangle}{\epsilon_a \pm \hbar\omega - \epsilon_r}$$

RPAE - Time Dependent HF