AULA 21

O Método Hartree-Fock

n férmions interagentes

$$\mathcal{H} = \sum_{\alpha\alpha'} b_\alpha^+ \langle\alpha| H_0 |\alpha'\rangle b_{\alpha'} + \frac{1}{2}\sum_{\substack{\alpha\beta \\ \alpha'\beta'}} b_\alpha^+ b_\beta^+ \langle\alpha\beta|V|\alpha'\beta'\rangle b_{\beta'} b_{\alpha'}$$

a essência do método

está na aproximação do ket por

$$|\Psi_0\rangle = a_n^+ a_{n-1}^+ \dots a_2^+ a_1^+ |0\rangle$$

e procurar uma base $\{|i\rangle\}$ que

minimiza a energia

NA nova base $\mathcal{H} = \sum_{i\ell} a_i^+ \langle i|H_0|\ell\rangle a_\ell + \frac{1}{2}\sum_{qrst} a_q^+ a_r^+ \langle qr|V|st\rangle a_t a_s$

Um passo posterior é "Interações de Configurações)

expandido $|\Psi\rangle$ em termos de $|\Psi_0\rangle$
e coisas do tipo:

$a_j^+ a_k |\Psi_0\rangle$ (excitações simples)

<u>variações</u>

procuramos por $a_k^+ + \delta a_k^+ = \sum_j a_j^+ \delta_{jk} + i\sum a_j^+ \varepsilon_{jk}$

VARIAÇÃO

transformação unitária

ou seja

$$\delta a_k^+ = i \sum_j a_j^+ \varepsilon_{jk} \qquad |\varepsilon_{jk}| \ll 1$$

matriz Hermiteana

se $\langle 0 | a_k a_k^+ | 0 \rangle = 1$

$$\langle 0 | \left(a_k - i\sum_\gamma a_\gamma \varepsilon_{\gamma k}^*\right)\left(a_k^+ + i\sum_\gamma a_\gamma^+ \varepsilon_{\gamma k}\right) | 0 \rangle$$

$$= 1 + i\sum_\gamma \langle \,| a_k a_\gamma^+ \varepsilon_{\gamma k} - a_\gamma a_k^+ \varepsilon_{\gamma k}^* |\, \rangle + O(\varepsilon^2)$$

$$= 1 - i\sum_\gamma \left(\delta_{k\gamma}\, \underbrace{\varepsilon_{\gamma k}^* - \delta_{\gamma k}\, \varepsilon_{\gamma k}}_{\text{exige apenas } \varepsilon_{kk}^* = \varepsilon_{kk}}\right) = 1 + \varepsilon^2$$

Assim defina $|\delta \Psi_{\gamma k}\rangle = \varepsilon_{\gamma k}\, a_\gamma^+ a_k |\Psi_0\rangle$

$\hookrightarrow$ destrói o que está na posição k

$\downarrow$

variações em $|\Psi_0\rangle$ pode ser realizada como combinações lineares de

da mesma forma

$$\langle \delta \Psi_{\gamma k}| = \varepsilon_{\gamma k}^* \langle \Psi_0 | a_k^+ a_\gamma$$

$$\varepsilon_{\gamma k}\, a_\gamma^+ a_k$$

$\uparrow$ aniquila 1 fermion do nível ocupado ($k \leq n$)

$\downarrow$

cria em um desocupado ($\gamma \geq n+1$)

$\gamma = k$ pura irrelevante (mesmo $|\Psi_0\rangle$)

note (troque k e γ)

$$|\delta \Psi_{k\gamma}\rangle = \varepsilon_{k\gamma}\, a_k^+ a_\gamma |\Psi_0\rangle = 0$$

$\hookrightarrow$ nível desocupado

a condição $\therefore$ "$\varepsilon_{k\gamma}^* = \varepsilon_{\gamma k}$" pode ser ignorada"

$$\delta \langle \mathcal{H} \rangle = 0$$

obs:

$$\langle \mathcal{H} \rangle = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

$$\delta \langle \mathcal{H} \rangle = 0 = \frac{\delta\left(\langle \Psi_0 | H | \Psi_0 \rangle\right) \langle \Psi_0 | \Psi_0 \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \, \delta\left(\langle \Psi_0 | \Psi_0 \rangle\right)}{\langle \Psi_0 | \Psi_0 \rangle^2}$$

$$\left(\langle \delta \Psi_0 | H | \Psi_0 \rangle + \langle \Psi_0 | H | \delta \Psi_0 \rangle\right) \langle \Psi_0 | \Psi_0 \rangle$$

$$- \langle \Psi_0 | H | \Psi_0 \rangle \left(\langle \delta \Psi_0 | \Psi_0 \rangle + \langle \Psi_0 | \delta \Psi_0 \rangle\right) = 0$$

$$\boxed{\begin{aligned}&\langle \delta \Psi_0 | H | \Psi_0 \rangle \langle \Psi_0 | \Psi_0 \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \langle \delta \Psi_0 | \Psi_0 \rangle + \\ &\langle \Psi_0 | H | \delta \Psi_0 \rangle \langle \Psi_0 | \Psi_0 \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \langle \Psi_0 | \delta \Psi_0 \rangle = 0\end{aligned}}$$

$$\langle \Psi_0 | H | \delta \Psi_0 \rangle^* = \left(\langle \delta \Psi_0 | H^+ | \Psi_0 \rangle^*\right)^* = \langle \delta \Psi_0 | H | \Psi_0 \rangle$$

é suficiente (considere $\langle \delta\Psi |$ e $| \delta \Psi \rangle$ independentes) tomar:

$$\boxed{\langle \delta \Psi_0 | \mathcal{H} | \Psi_0 \rangle \langle \Psi_0 | \Psi_0 \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \langle \delta \Psi_0 | \Psi_0 \rangle = 0}$$

lembre $\quad | \delta \Psi_0 \rangle = \varepsilon_{jk} \, a_j^+ a_k | \Psi_0 \rangle \quad (j \neq k)$

j → desocupado, k → ocupado

$$\therefore \langle \delta \Psi_0 | \Psi_0 \rangle = 0 \quad \left(\varepsilon_{jk}^* \langle \Psi_0 | a_k^+ \underbrace{a_j | \Psi_0 \rangle}_{0}\right)$$

$\therefore$ precisamos ter

$$\boxed{\langle \delta \Psi_\nu | \mathcal{H} | \Psi_\nu \rangle = 0}$$

ε^*_{jk} $\langle \Psi_\nu | a_k^+ a_j H | \Psi_\nu \rangle = 0$ e $\therefore$

$$\langle \Psi_\nu | a_k^+ a_j \left(\sum_{il} \langle i | H_0 | l \rangle a_i^+ a_l \right) | \Psi_\nu \rangle$$

$$+ \langle \Psi_\nu | a_k^+ a_j \left(\frac{1}{2} \sum_{\substack{qr \\ st}} a_q^+ a_r^+ a_s a_t \langle qr | V | ts \rangle \right) | \Psi_\nu \rangle = 0$$

$$\sum_{il} \langle i | H_0 | l \rangle \langle \Psi_\nu | a_k^+ a_j a_i^+ a_l | \Psi_\nu \rangle$$

$$+ \frac{1}{2} \sum_{\substack{qr \\ st}} \langle qr | V | ts \rangle \langle \Psi_\nu | a_k^+ a_j a_q^+ a_r^+ a_s a_t | \Psi_\nu \rangle = 0$$

faz o j andar p/ direita
↳ desocupado

$$\sum_{il} \langle i | H_0 | l \rangle \langle \Psi_\nu | a_k^+ (\delta_{ij} - a_i^+ a_j) a_l | \Psi_\nu \rangle$$

$$+ \frac{1}{2} \sum_{\substack{qr \\ st}} \langle qr | V | ts \rangle \langle \Psi_\nu | a_k^+ (\delta_{jq} - a_q^+ a_j) a_r^+ a_s a_t | \Psi_\nu \rangle = 0$$

$$\sum_{l} \langle j | H_0 | l \rangle \langle \Psi_\nu | a_k^+ a_l | \Psi_\nu \rangle + \sum_{il} \langle i | H_0 | l \rangle \langle \Psi_\nu | a_k^+ a_i^+ a_l \underbrace{a_j | \Psi_\nu \rangle}_{0}$$

note "l" precisa ser ocupado e $k=l$

$$+ \frac{1}{2} \sum_{rst} \langle jr | V | ts \rangle \langle \Psi_\nu | a_k^+ a_r^+ a_s a_t | \Psi_\nu \rangle - \frac{1}{2} \sum_{\substack{qr \\ st}} \langle qr | V | ts \rangle \langle \Psi_\nu | a_k^+ a_q^+ a_j a_r^+ a_s a_t | \Psi_\nu \rangle$$

$$\therefore \langle p|H_0|k\rangle - \frac{1}{2}\sum_{rst} \langle pr|v|ts\rangle \langle \Psi_0| a_r^\dagger a_k^\dagger a_s a_t |\Psi_0\rangle$$

$$-\frac{1}{2}\sum_{\substack{qr\\st}} \langle qr|v|ts\rangle \langle \Psi_0| a_k^\dagger a_q^\dagger \left(\delta_{pr} - a_r^\dagger a_p\right) a_s a_t |\Psi_0\rangle = 0$$

$$\langle p|H_0|k\rangle - \frac{1}{2}\sum_{rst} \langle pr|v|ts\rangle \langle \Psi_0| a_r^\dagger (\delta_{ks} - a_s a_k^\dagger) a_t |\Psi_0\rangle$$

$$-\frac{1}{2}\sum_{qst} \langle qp|v|ts\rangle \langle \Psi_0| a_k^\dagger a_q^\dagger a_s a_t |\Psi_0\rangle$$

com até aqui)

$$+\frac{1}{2}\sum_{\substack{qr\\st}} \langle qr|v|ts\rangle \langle \Psi_0| a_k^\dagger a_q^\dagger a_r^\dagger a_s a_t \underbrace{a_p |\Psi_0\rangle}_{0} = 0$$

$$\langle p|H_0|k\rangle - \frac{1}{2}\sum_{rt} \langle pr|v|tk\rangle \langle \Psi_0| a_r^\dagger a_t |\Psi_0\rangle$$

$$+\frac{1}{2}\sum_{rst} \langle pr|v|ts\rangle \langle \Psi_0| a_r^\dagger a_s a_k^\dagger a_t |\Psi_0\rangle$$

$$+\frac{1}{2}\sum_{qst} \langle qp|v|ts\rangle \langle \Psi_0| a_q^\dagger a_k^\dagger a_s a_t |\Psi_0\rangle = 0$$

$$\langle p|H_0|k\rangle - \frac{1}{2}\sum_{t}^{\text{ocupados}} \langle pt|v|tk\rangle + \frac{1}{2}\sum_{qst} \langle qp|v|ts\rangle$$

$$+\frac{1}{2}\sum_{rst} \langle pr|v|ts\rangle \langle \Psi_0| a_r^\dagger a_s (\delta_{kt} - a_t \underbrace{a_k^\dagger) |\Psi_0\rangle}_{0} + \langle \Psi_0| a_q^\dagger (\delta_{ks} - a_s a_k^\dagger) a_t |\Psi_0\rangle = 0$$

$$\langle p|H_0|k\rangle - \frac{1}{2}\sum_{t}^{\text{ocupados}} \langle pt|v|tk\rangle + \frac{1}{2}\sum_{qt} \langle qp|v|tk\rangle \langle \Psi_0| a_q^\dagger a_t |\Psi_0\rangle$$

δ_{qt} ocupados

$$-\frac{1}{2}\sum_{qst} \langle qp|v|ts\rangle \langle \Psi_0| a_q^\dagger a_s a_k^\dagger a_t |\Psi_0\rangle$$

$$+\frac{1}{2}\sum_{rs} \langle pr|v|ks\rangle \langle \Psi_0| a_r^\dagger a_s |\Psi_0\rangle = 0$$

$$\langle r|H_0|k\rangle - \frac{1}{2}\sum_t \langle rt|V|tk\rangle + \frac{1}{2}\sum_t \langle tr|V|tk\rangle$$

$$-\frac{1}{2}\sum_{qst}\langle q r|V|ts\rangle\langle \Psi_0|a_q^+ a_s(\delta_{kt} - \underbrace{a_t a_k^+)|\Psi_0\rangle}_{0}$$
$$+\frac{1}{2}\sum_r \langle rr|V|kr\rangle$$

$$\langle r|H_0|k\rangle - \frac{1}{2}\sum_t \langle rt|V|tk\rangle + \frac{1}{2}\sum_t \langle rt|V|\underbrace{kt}_{\text{troquei ambos}}\rangle$$

$$-\frac{1}{2}\sum_{qs}\langle qr|V|ks\rangle\underbrace{\langle\Psi_0|a_q^+ a_s|\Psi_0\rangle}_{\delta_{sq}} + \frac{1}{2}\sum_r \langle rr|V|kr\rangle = 0$$

$$\boxed{\langle r|H_0|k\rangle - \underbrace{\sum_t \langle rt|V|tk\rangle}_{\text{termo de troca}} + \underbrace{\sum_t \langle rt|V|kt\rangle}_{\text{termo direto}} = 0}$$

$r \geq n+1$ $\quad k \leq n$

$$\langle \underset{\text{desocupado}}{r}| \left\{ H_0|k\rangle + \sum_t \sum_p |p\rangle\left(\langle pt|V|kt\rangle - \langle pt|V|tk\rangle\right)\right\} = 0$$

se resolver $\boxed{H_{HF}|\underset{\text{ocupado}}{m}\rangle = \varepsilon_m|m\rangle}$ temos $\left(\langle \underset{\text{desocupado}}{r}|H_F|m\rangle = \varepsilon_m\langle r|\underset{\text{ocupado}}{m}\rangle = 0\right)$

$$H_{HF}|m\rangle = H_0|m\rangle + \sum_{p=1}|p\rangle\sum_{t=1}^{ocup}\left[\langle pt|V|mt\rangle - \langle pt|V|tm\rangle\right] = \varepsilon_m|m\rangle$$

mostre $H_F^+ = H_F$ e $\therefore$ autokets com autovalores distintos são ortogonais.

Se na base original $\langle \alpha\beta | V | \alpha'\beta' \rangle = V_{\alpha\beta}\, \delta_{\alpha\alpha'}\, \delta_{\beta\beta'}$

$$\langle pt|V|mt\rangle - \langle pt|V|tm\rangle = \sum_{\substack{\alpha\beta \\ \alpha'\beta'}} \langle pt|\alpha\beta\rangle \langle \alpha\beta|V|\alpha'\beta'\rangle \langle \alpha'\beta'| \left(|mt\rangle - |tm\rangle \right)$$

$$= \sum_{\substack{\alpha\beta \\ \alpha'\beta'}} \langle pt|\alpha\beta\rangle V_{\alpha\beta}\, \delta_{\alpha\alpha'}\, \delta_{\beta\beta'} \left(\langle \alpha'\beta'|mt\rangle - \langle \alpha'\beta'|tm\rangle \right)$$

$$= \sum_{\alpha\beta} \langle pt|\alpha\beta\rangle V_{\alpha\beta} \left(\langle \alpha\beta|mt\rangle - \langle \alpha\beta|tm\rangle \right)$$

$$= \sum_{\alpha\beta} \langle p|\alpha\rangle \langle t|\beta\rangle V_{\alpha\beta} \left(\langle \alpha|m\rangle \langle \beta|t\rangle - \langle \alpha|t\rangle \langle \beta|m\rangle \right)$$

$$H_{HF}|m\rangle = H_0|m\rangle + \underbrace{\sum_{p=1}^{\infty} |p\rangle\langle p|}_{1} \left\{ \sum_{t=1}^{ocup} \sum_{\alpha\beta} |\alpha\rangle \langle t|\beta\rangle V_{\alpha\beta} \left(\langle \alpha|m\rangle\langle \beta|t\rangle - \langle \alpha|t\rangle \langle \beta|m\rangle \right) \right\}$$

$$= H_0|m\rangle + \sum_{t=1}^{ocup} \sum_{\alpha\beta} |\alpha\rangle \langle t|\beta\rangle V_{\alpha\beta} \left(\langle \beta|t\rangle \langle \alpha|m\rangle - \langle \alpha|t\rangle \langle \beta|m\rangle \right)$$

$$= \varepsilon_m |m\rangle$$

Antes de prosseguir

note $\langle m|\varepsilon_m|m\rangle = \varepsilon_m = \langle m|H_0|m\rangle$

$$\sum_{p=1}^{\infty} \langle m|p\rangle \sum_{t=1}^{ocup} \left[\langle pt|V|mt\rangle - \langle pt|V|tm\rangle \right]$$

$$= \langle m|H_0|m\rangle + \sum_{t=1}^{ocup} \left[\langle mt|V|mt\rangle - \langle mt|V|tm\rangle \right]$$

A escolha dos estados ocupados $|t\rangle$ não é arbitrária os primeiros n estados com ε_m mais baixos correspondem ao mínimo de $\langle \mathcal{H} \rangle$

mas note que

$$E_\nu = \langle \mathcal{H} \rangle = \langle \Psi_\nu | \mathcal{H} | \Psi_\nu \rangle$$

$$= \langle \Psi_\nu | \sum_{i,l} \langle i | H_0 | l \rangle a_i^\dagger a_l | \Psi_\nu \rangle$$

"l" precisa ser ocupado e $i = l$ (faça $i = l = k$)

$$+ \frac{1}{2} \sum_{qrst} \langle qr | V | st \rangle \langle \Psi_\nu | a_q^\dagger a_r^\dagger a_t a_s | \Psi_\nu \rangle$$

$s \neq t$ $q \neq r$ $s = r$, $t = q$ ou $s = q$, $t = r$

$$= \sum_{k}^{ocup} \langle k | H_0 | k \rangle + \frac{1}{2} \sum_{\substack{qr \\ q \neq r}} \langle qr | V | rq \rangle \langle \Psi_\nu | a_q^\dagger \underbrace{a_r^\dagger a_q}_{\delta_{qr} - a_q a_r^\dagger} a_r | \Psi_\nu \rangle$$

zero pois $q \neq r$

$$+ \frac{1}{2} \sum_{\substack{qr \\ q \neq r}} \langle qr | V | qr \rangle \langle \Psi_\nu | a_q^\dagger a_r^\dagger a_r a_q | \Psi_\nu \rangle$$

$(-)(-)$

assim:

$$E_\nu = \overbrace{\sum_{k}^{ocup} \langle k | H_0 | k \rangle + \frac{1}{2} \sum_{\substack{k,l \\ k \neq l}} \langle kl | V | kl \rangle - \frac{1}{2} \sum_{\substack{k,l \\ k \neq l}} \langle kl | V | lk \rangle}^{\text{não é soma de } \varepsilon_k}$$

$$= \frac{1}{2} \sum_{k=1}^{n} \left[\varepsilon_k + \langle k | H_0 | k \rangle \right] = \sum_{k} \varepsilon_k - \frac{1}{2} \sum_{\substack{l,k \\ l \neq k}}^{ocup} \left[\langle kl | V | kl \rangle - \langle kl | V | lk \rangle \right]$$

Como resolver a equação de Hartree-Fock?

olhe p/

$$H_{HF}|m\rangle = \varepsilon_m|m\rangle$$

$$\boxed{H_0|m\rangle + \sum_{t=1}^{n}\sum_{\alpha\beta}|\alpha\rangle\langle t|\beta\rangle V_{\alpha\beta}\left[\langle\beta|t\rangle\langle\alpha|m\rangle - \langle\alpha|t\rangle\langle\beta|m\rangle\right] = \varepsilon_m|m\rangle}$$

p/ achar $|m\rangle$ precisa saber todos os $|t\rangle$'s

"SCF"

Vamos reescrever a equação acima na representação que diagonaliza V

$$\langle\alpha|H_0|\sum|\beta\rangle\langle\beta|m\rangle + \sum_{t=1}^{n}\sum_{\beta}\langle t|\beta\rangle V_{\alpha\beta}\langle\beta|t\rangle\langle\alpha|m\rangle$$

$$-\sum_{t=1}^{n}\sum_{\beta}\langle t|\beta\rangle V_{\alpha\beta}\langle\alpha|t\rangle\langle\beta|m\rangle = \varepsilon_m\langle\alpha|m\rangle$$

$$\sum_{\beta}\left[\langle\alpha|H_0|\beta\rangle\langle\beta|m\rangle + \sum_{t=1}^{n}\langle t|\beta\rangle V_{\alpha\beta}\left(\langle\beta|t\rangle\langle\alpha|m\rangle - \langle\alpha|t\rangle\langle\beta|m\rangle\right)\right]$$

$$= \varepsilon_m\langle\alpha|m\rangle$$

o que é H_0? e V para 1 átomo

que tal $H_0 = \frac{p^2}{2m} - \frac{Ze^2}{r}$

$$V(\vec{r}\sigma, \vec{r}'\sigma') = \frac{e^2}{|\vec{r}-\vec{r}'|} = \langle \vec{r}\sigma | v | \vec{r}\sigma' \rangle$$

$|\alpha\rangle$ e $|\beta\rangle$ serão $|\vec{r}\sigma\rangle$ e $|\vec{r}'\sigma'\rangle$

assim $\langle \alpha | m \rangle = \langle \vec{r}\sigma | m \rangle = \psi_m(\vec{r}\sigma)$ função de uma-partícula na representação das coordenadas

mas

$$\langle \vec{r}\sigma | H_0 | \vec{r}'\sigma' \rangle = \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right) \delta(\vec{r}-\vec{r}') \delta_{\sigma\sigma'}$$

lembre $\sum_{\beta} \to \sum_{\sigma'} \int d^3r'$

$$\sum_{\sigma'} \int d^3r' \Big\{ \langle \vec{r}\sigma | H_0 | \vec{r}'\sigma' \rangle \langle \vec{r}'\sigma' | m \rangle$$

$$+ \sum_{t=1}^{n} \langle t | \vec{r}'\sigma' \rangle \frac{e^2}{|\vec{r}-\vec{r}'|} \Big(\langle \vec{r}'\sigma' | t \rangle \langle \vec{r}\sigma | m \rangle - \langle \vec{r}\sigma | t \rangle \langle \vec{r}'\sigma' | m \rangle \Big)$$

$$= \varepsilon_m \langle \vec{r}\sigma | m \rangle$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_m(\vec{r}\sigma) - \frac{Ze^2}{r} \psi_m(\vec{r}\sigma) + e^2 \sum_{t=1}^{n} \sum_{\sigma'} \int d^3r' \psi_t^*(\vec{r}'\sigma') \frac{1}{|\vec{r}-\vec{r}'|} \psi_t(\vec{r}'\sigma') .$$

$$\psi_m(\vec{r}\sigma) - e^2 \sum_{t=1}^{n} \sum_{\sigma'} \int d^3r' \, \psi_t^*(\vec{r}'\sigma') \frac{1}{|\vec{r}-\vec{r}'|} \psi_m(\vec{r}'\sigma') \, \psi_t(\vec{r}\sigma) = \varepsilon_m \psi_m(\vec{r}\sigma)$$