Résumé

$$\sum_{i=1}^{n} O_i \quad |\alpha_1\rangle|\alpha_2\rangle|\alpha_3\rangle\ldots|\alpha_n\rangle$$

$$\langle\alpha'|O_i|\alpha\rangle = \langle\alpha'|\alpha\rangle\langle\alpha|O_i|\alpha\rangle$$

$$\underbrace{\sum_{i=1}^{n}\langle\alpha_i|O_i|\alpha_i\rangle}\Big(\langle\alpha'_1|\underbrace{\langle\alpha'_2|\ldots\langle\alpha'_n|}|\underbrace{\alpha_1\rangle|\alpha_2\rangle}\ldots|\alpha_n\rangle\Big)$$

$$C^+_\alpha C_\alpha$$

$$\sum_\alpha \langle\alpha|O|\alpha\rangle C^+_\alpha C_\alpha$$

$$|\alpha\rangle = \int dx\, |x\rangle\langle x|\alpha\rangle$$

$$C^+_\alpha = \int dx\, \Psi^+(x)\langle x|\alpha\rangle$$

$$\int dx\, dy\; \Psi^+(y)\langle y|O|x\rangle\Psi(x)$$

$$\langle y|O|x\rangle = \delta(x-y)$$

$$\int dx\; \Psi^+(x)\Psi(x)$$

Exercices:

$$\int dx\,dy\; \Psi^+(y)\, \langle y|O|x\rangle\, \Psi(x)$$

i) O est un potentiel à 1 corps.

$$\langle y|V|x\rangle = V(x)\,\delta(x-y)$$

$$\int dx\; \Psi^+(x)\, V(x)\, \Psi(x)$$

ii)

$$\langle y|\frac{P^2}{2m}|x\rangle = \int \frac{dp}{2\pi} \langle y|\frac{P^2}{2m}|p\rangle\langle p|x\rangle$$

$$= \int \frac{dp}{2\pi} \boxed{\frac{\hbar^2 p^2}{2m}} \langle y|p\rangle\langle p|x\rangle$$

$$= \int \frac{dp}{2\pi} \boxed{\frac{\hbar^2 p^2}{2m}}\, e^{ipy-ipx}$$

$$= \int \boxed{\frac{dp}{2\pi}}\, \frac{\hbar^2}{2m} \left(-\frac{\partial^2}{\partial x^2}\right) e^{ip(y-x)}$$

$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\, \delta(x-y)$$

$$\int dx\,dy\; \Psi^+(y) \left(\frac{-\hbar^2}{2m}\right) \frac{d^2}{dx^2}\, \delta(x-y)\, \Psi(x)$$

$$-\frac{\hbar^2}{2m} \int dx\; \Psi^+(x)\, \frac{d^2}{dx^2}\, \Psi(x)$$

$$\boxed{H = \int d^3r\, \psi^+(\vec{r})\, D\, \psi(\vec{r})}$$

$$D = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

$$D\varphi_n(\vec{r}) = E_n \varphi_n(\vec{r})$$

$$\boxed{\psi^+(\vec{r}) = \sum_n c_n^+ \varphi_n^*(\vec{r})} \leftarrow$$

$$|\vec{r}\rangle = \sum_n |n\rangle\langle n|\vec{r}\rangle \leftarrow$$

$$\langle \vec{r}|n\rangle = \varphi_n(\vec{r})$$

$$D\psi = D\sum_n c_n \varphi_n(\vec{r})$$

$$= \sum_n c_n E_n \varphi_n(\vec{r})$$

$$\psi^+ D\psi = \sum_{n'n} c_{n'}^+ \varphi_{n'}^*(\vec{r})\, E_n c_n \varphi_n(\vec{r})$$

$$\sum_{n'n} E_n c_{n'}^+ c_n \int d^3r\, \varphi_{n'}^*(\vec{r})\varphi_n(\vec{r})$$

$$= \sum_{n'n} E_n c_{n'}^+ c_n\, \delta_{n,n'}$$

$$= \sum_n E_n c_n^+ c_n$$

$$|\psi\rangle = c_{n_1}^+ c_{n_2}^+ |0\rangle$$

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$$|n\rangle = \int d^3r\, |\vec{r}\rangle \boxed{\langle \vec{r} | n \rangle}$$

$$c^{+}_{n} = \int d^3r\, \psi^{+}(\vec{r}) \boxed{\varphi_n(\vec{r})}$$

$$c_n = \int d^3r'\, \psi(\vec{r}')\, \varphi_n^{*}(\vec{r}')$$

$$[c_n, c_m^{+}] =$$

$$\int d^3r\, d^3r'\, \varphi_n^{*}(\vec{r}')\, \varphi_m(\vec{r})$$

$$\underbrace{\boxed{[\psi(\vec{r}')\psi^{+}(\vec{r}) - \psi^{+}(\vec{r})\psi(\vec{r}')]}}_{\delta^3(r-r')}$$

$$= \int d^3r\, d^3r'\, \varphi_n^{*}(\vec{r}')\, \varphi_m(\vec{r})\, \underline{\delta(\vec{r}-\vec{r}')}$$

$$= \delta_{m,n} = \int d^3r\, \varphi^{*}_n(\vec{r})\, \varphi_m(\vec{r})$$

$$U_{rn} = \langle \vec{r} | n \rangle$$

$$U^{+}_{mr} = \langle n | \vec{r} \rangle$$

$$\int d^3r\, U^{+}_{mr}\, U_{rn} = \delta_{mn}$$

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5.? Opérateurs à 2 corps.

exemple 1ère quant.

$$\frac{1}{2}\sum_{\substack{i=1\\ j=1\\ i\neq j}}^{n,n} V(x_i - x_j) \quad \text{énergie potentielle}$$

Sans antisymétrie

$$\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \int d\vec{x}_i\, d\vec{x}_j \, \frac{|\Psi_i(\vec{x}_i)|^2 e \; e\, |\Psi(x_j)|^2}{|\vec{x}_i - \vec{x}_j|}$$

Base diagonale :

$$\langle \alpha' | \langle \beta' | \, V \, | \alpha \rangle \, | \beta \rangle$$

$$= V_{\alpha\beta} \, \langle \alpha' | \alpha \rangle \langle \beta' | \beta \rangle$$

ex.

$$\langle x' | \langle y' | \, V \, | x \rangle \, | y \rangle$$

$$= V(x - y) \, \langle x' | x \rangle \, \langle y' | y \rangle$$

$$\langle \alpha'_1 | \langle \alpha'_2 | \ldots \langle \alpha'_n |$$

$$\frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} V_{ij} \, | \alpha_1 \rangle | \alpha_2 \rangle \ldots | \alpha_n \rangle$$

$$= \boxed{\frac{1}{2} \sum_{\substack{\alpha_i \alpha_j \\ i \neq j}} V_{\alpha_i \alpha_j}} \left(\langle \alpha'_1 | \langle \alpha'_2 | \ldots \langle \alpha'_n | \, | \alpha_1 \rangle \ldots | \alpha_n \rangle \right)$$

$$= \frac{1}{2} \sum_{\substack{\alpha_i \alpha_j \\ i \neq j}} V_{\alpha_i \alpha_j} \left(\langle \overset{1}{\alpha'_1} \ldots \overset{1}{\alpha'_n} | \overset{1}{\alpha_1} \ldots \overset{1}{\alpha_n} \rangle \right)$$

$$= \langle \alpha'_1 \ldots \alpha'_n | \, \frac{1}{2} \sum_{\alpha\beta} V_{\alpha\beta} \left(c^+_\alpha c_\alpha c^+_\beta c_\beta - \delta_{\alpha\beta} c^+_\alpha c_\alpha \right) | \alpha_1 \ldots \alpha_n \rangle$$

$$V_{ij} \, | \alpha_1 \rangle | \alpha_2 \rangle \ldots \ldots | \alpha_n \rangle$$

$$V_{\alpha_i \alpha_j} | \alpha_1 \rangle | \alpha_2 \rangle \ldots \ldots | \alpha_n \rangle$$

$$c_\alpha^+ c_\alpha c_\beta^+ c_\beta - \delta_{\alpha\beta} c_\alpha^+ c_\alpha$$

$$c_\alpha^+ \left(\delta_{\alpha\beta} \pm c_\beta^+ c_\alpha \right) c_\beta - \delta_{\alpha\beta} c_\alpha^+ c_\alpha$$

$$= \pm c_\alpha^+ c_\beta^+ c_\alpha c_\beta$$

$$= c_\alpha^+ c_\beta^+ c_\beta c_\alpha$$

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Dans la base diagonale:

Opérateur à 2 corps

$$\frac{1}{2}\sum_{\alpha\beta} V_{\alpha\beta}\, c^+_\alpha c^+_\beta c_\beta c_\alpha$$

$$c^+_\alpha = \int dx'\, \psi^+(x')\, \langle x'|\alpha\rangle$$

$$= \frac{1}{2}\sum_{\alpha\beta} V_{\alpha\beta} \int dx'\, dy'\, dx\, dy\, \psi^+(x')\langle x'|\alpha\rangle$$

$$\psi^+(y')\langle y'|\beta\rangle\langle\beta|x\rangle\psi(x)\,\langle\alpha|y\rangle\psi(y)$$

Note:

$$\frac{1}{2}\sum_{\alpha\beta} \langle x'|\alpha'\rangle\langle y'|\beta'\rangle V_{\alpha\beta}\langle\beta|x\rangle\langle\alpha|y\rangle$$

$$= \frac{1}{2}\langle x'|\langle y'|V|y\rangle|x\rangle$$

$$\boxed{\begin{array}{c}\frac{1}{2}\int dx'dy'dxdy\, \langle x'|\langle y'|V|y\rangle|x\rangle \\ \psi^+(x')\,\psi^+(y')\,\psi(x)\,\psi(y)\end{array}}$$

$$\langle x'|\langle y'|V|y\rangle|x\rangle = V(x-y)\underbrace{\langle x'|y\rangle}_{\delta(x'-y)}\underbrace{\langle y'|x\rangle}_{\delta(y'-x)}$$

$$= \boxed{\frac{1}{2}\int dx\,dy\, V(x-y)\,\psi^+(y)\,\psi^+(x)\,\psi(x)\,\psi(y)}$$

$$\langle\alpha'|\langle\beta'|V|\alpha\rangle|\beta\rangle = V_{\alpha\beta}\,\langle\alpha'|\alpha\rangle\langle\beta'|\beta\rangle$$

$$= V_{\alpha'\beta',\alpha\beta}$$

Formel :

$$H = \sum_{\sigma} \int d^3r \; \Psi^{+}_{\sigma}(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \Psi_{\sigma}(r)$$

Méc. class :

$$\dot{p} = -\frac{\partial H}{\partial q} \qquad \dot{q} = \frac{\partial H}{\partial p} \qquad \boxed{[Q, P] = i\hbar}$$

Essayons $\boxed{q \rightarrow \Psi}$

$$\dot{p} = -\frac{\partial H}{\partial q} = -\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \Psi^{+}$$

$$= i\hbar \frac{\partial \Psi^{+}}{\partial t}$$

$$\dot{p} \rightarrow i\hbar \frac{\partial \Psi^{+}}{\partial t}$$

$$\boxed{p \rightarrow i\hbar \Psi^{+}}$$

$$\left[\Psi_{r}, i\hbar \Psi^{+}_{r'} \right] = \delta_{r,r'} \, i\hbar$$

$$\left[\Psi(r), \Psi^{+}(r') \right] = \delta(\vec{r} - \vec{r}')$$

Approximation de Hartree-Fock

"Champ moyen" pour les systèmes à N particules

Intuitif:

Une particule   Hartree:

$$-\frac{\hbar^2}{2m}\nabla^2\varphi_n(\vec{r}) + \left[V(r) + U(r)\right]\varphi_n(r) = \epsilon_n\varphi_n(r)$$

Particules en interaction:

Interaction de Coulomb

$$\rightarrow U(\vec{r}) = \int d^3r' \, \frac{e^2}{|\vec{r}-\vec{r}'|}\rho(\vec{r}')$$

$$= \int d^3r' \, \frac{e^2}{|\vec{r}-\vec{r}'|}\sum_{n \text{ occupés}} |\varphi_n(\vec{r}')|^2$$

Principe variationnel (Ritz)

$$\boxed{\langle \Psi | H | \Psi \rangle \geqslant \langle \Psi_0 | H | \Psi_0 \rangle}$$

si $\langle \Psi | \Psi \rangle = 1 \leftarrow$

$$H | \Psi \rangle = \sum_{i=0}^{\infty} a_i | \Psi_i \rangle E_i$$

$$\langle \Psi | H | \Psi \rangle = \sum_{i=0}^{\infty} E_i |a_i|^2 \geqslant E_0$$

$$\geqslant \sum_{i=0}^{\infty} E_0 |a_i|^2$$

$$= E_0 \sum_{i=0}^{\infty} |a_i|^2$$

$$= E_0$$

$$H = \int d^3r\, \psi^{*}(\vec{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi(\vec{r})$$

$$+ \frac{1}{2}\int d^3r\, d^3r'\, \psi^{+}(\vec{r})\, \psi^{+}(\vec{r}\,')\, U(|\vec{r}-\vec{r}\,'|)\, \psi(\vec{r}\,')\, \psi(\vec{r})$$

$$\boxed{|\Phi_0\rangle = a_1^{+} a_2^{+} \cdots a_N^{+} |0\rangle}$$

$$\boxed{\psi^{+}(\vec{r}) = \sum_n a_n^{+} \varphi_n^{*}(\vec{r})}$$

$$\boxed{\psi(\vec{r}) = \sum_n \varphi_n(r)\, a_n}$$

$$|\phi\rangle = \sum_i C_i |\phi_i\rangle$$

À faire

$$\frac{\partial}{\partial \varphi_n(r_i)} \langle \phi_0 | H | \phi_0 \rangle = 0$$

Contrainte

$$\int d^3r\, \varphi_n^{*}(r)\, \varphi_m(r) = \delta_{nm}$$