Tuesday, November 19, 2024 9:54 PM

Free interacting electrons

2nd quantization formalism

$$\Psi(\vec{r}_1,\vec{r}_2) = \Big(|\psi_{\alpha_1}(\vec{r}_1)\rangle|\psi_{\alpha_2}(\vec{r}_2)\rangle - |\psi_{\alpha_2}(\vec{r}_1)\rangle|\psi_{\alpha_1}(\vec{r}_2)\rangle\Big)$$

Slater

$$\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = \frac{1}{\sqrt{N}}\begin{vmatrix} |\psi_{\alpha_1}(\vec{r}_1)\rangle & |\psi_{\alpha_2}(\vec{r}_1)\rangle & |\psi_{\alpha_3}(\vec{r}_1)\rangle & \cdots & |\psi_{\alpha_N}(\vec{r}_1)\rangle \\ |\psi_{\alpha_1}(\vec{r}_2)\rangle & |\psi_{\alpha_2}(\vec{r}_2)\rangle & |\psi_{\alpha_3}(\vec{r}_2)\rangle & \cdots & |\psi_{\alpha_N}(\vec{r}_2)\rangle \\ & & \vdots & & \\ |\psi_{\alpha_1}(\vec{r}_N)\rangle & |\psi_{\alpha_2}(\vec{r}_N)\rangle & |\psi_{\alpha_3}(\vec{r}_N)\rangle & \cdots & |\psi_{\alpha_N}(\vec{r}_N)\rangle \end{vmatrix}$$

cumbersome

Occupation number representat

$$|\Psi\rangle = |n_{\alpha_1}, n_{\alpha_2}, n_{\alpha_3}, \ldots, n_{\alpha_N}\rangle$$

$|1_{\alpha_1}, 1_{\alpha_2}\rangle$; $|2_{\alpha_1}, 0_{\alpha_2}\rangle$ and so on.

$n = \begin{cases} 0 \\ 1 \end{cases} \forall \; \alpha_i$ jellium

$\alpha_i = \{\vec{k}_i \, \sigma_i\}$

Vacuum state $| \quad \rangle = |0\rangle$

Vacuum state $|00\ldots0) \equiv |0\rangle$

fiducial

$\hat{c}^\dagger_{\alpha_2}\,\hat{c}^\dagger_{\alpha_1}\,|0)$ and so on.

Fermionic commutation relation

$\rightarrow \underbrace{\hat{c}^\dagger_{\alpha_1}\hat{c}^\dagger_{\alpha_2}\,|0)} = |\psi)$

Order is important.

$\rightarrow \underbrace{\hat{c}^\dagger_{\alpha_2}\,\hat{c}^\dagger_{\alpha_1}\,|0)} = |\psi')$

$\hat{c}_{\alpha_1}\left(\hat{c}^\dagger_{\alpha_1}\hat{c}^\dagger_{\alpha_2}|0)\right) = |\phi)$

$\hat{c}_{\alpha_1}\left(\hat{c}^\dagger_{\alpha_2}\hat{c}^\dagger_{\alpha_1}|0)\right) = -|\phi)$

Prove on your own

$\left\{\hat{c}_\alpha, \hat{c}^\dagger_\beta\right\} = \delta_{\alpha,\beta}$ ← stem from the commutat relation

$\left[\hat{a}_\alpha, \hat{a}^\dagger_\beta\right] = \delta_{\alpha,\beta}$

$\rightarrow |\psi) = \hat{c}^\dagger_{\alpha_1}\hat{c}^\dagger_{\alpha_2}\hat{c}^\dagger_{\alpha_3}\ldots\hat{c}^\dagger_{\alpha_N}\,|0)$

$\underset{\text{annih.}}{\hat{c}_i}\,|\psi) = (-1)^{\nu_i}\,(n_{\alpha_i})\,|\ldots, n_{\alpha_i}-1, \ldots\rangle$ ←

$$\nu_i = \sum_{k=1}^{i-1} n_{\alpha_k}$$

annih.

$$\nu_i = \sum_{k=1} n_{\alpha_k}$$

$$\hat{c}_i^\dagger |\psi\rangle = (-1)^{\nu_i}(1-n_{\alpha_i})|\ \ldots, n_\alpha+1, \ldots\rangle$$

$$\underbrace{\hat{c}_i^\dagger c_i}_{\text{number operator on } \alpha_i \text{ state.}} |\psi\rangle = n_i$$

Prove on your own.

$$N = \sum_i \hat{c}_i^\dagger c_i = \sum_i n_i$$

2nd quantization form of operators

Ex 1 single ~~of~~ particle operator

$$\hat{A} \longrightarrow \sum_{\alpha,\beta} \langle\alpha|\hat{A}|\beta\rangle \hat{c}_\alpha^\dagger \hat{c}_\beta$$

$$\hat{p} \longrightarrow \sum_{\vec{p}_1,\vec{p}_2} \langle\vec{p}_1|\hat{p}|\vec{p}_2\rangle \hat{c}_{\vec{p}_1}^\dagger \hat{c}_{\vec{p}_2}$$

$$= \sum_{\vec{p}_1,\vec{p}_2} p_1 \langle\vec{p}_1|\vec{p}_2\rangle \hat{c}_{\vec{p}_1}^\dagger \hat{c}_{\vec{p}_2}$$

$$= \sum_{\vec{p}_1,\vec{p}_2} p_1 \delta_{\vec{p}_1,\vec{p}_2} \underbrace{\hat{c}_{\vec{p}_1}^\dagger \hat{c}_{\vec{p}_2}}_{n_{\vec{p}}}$$

$$= \sum_{\vec{p}} \underbrace{p}_{\text{eigenvalue}} \hat{c}_{\vec{p}}^\dagger \hat{c}_{\vec{p}}$$

$$f(\hat{p}) \longrightarrow \sum_{\vec{p}} f(p)\, \hat{c}_{\vec{p}}^\dagger \hat{c}_{\vec{p}}$$

$$f(\hat{p}) \longrightarrow \sum_{\vec{p}} f(p)\, \hat{c}^{\dagger}_{\vec{p}}\, c_{\vec{p}}$$

$$\boxed{\frac{\hat{p}^2}{2m} \longrightarrow \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m}\, \hat{C}^{\dagger}_{\vec{k}}\, C_{\vec{k}}}$$

K.E. term of all electrons

Ex 2 $\boxed{\hat{V}(\vec{r})}$

Field operators

$$\hat{\psi}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} e^{+i\vec{k}\cdot\vec{r}}\, \hat{C}_{\vec{k}}$$

annihilates a particle located at $\vec{r}$

analog $\Longleftarrow$

$$\hat{d}_i = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{+i\vec{k}\cdot\vec{r}}\, \hat{C}_{\vec{k}}$$

$$\hat{d}^{\dagger}_i = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}}\, \hat{C}^{\dagger}_{\vec{k}}$$

$\boxed{1}$

$$\hat{\psi}^{\dagger}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}}\, \hat{C}^{\dagger}_{\vec{k}}$$

$\boxed{2}$

$$\boxed{F_{\vec{k}} = \frac{1}{V(\vec{r})} \int d^3r\, f(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}} \quad \checkmark \quad \frac{1}{\sqrt{V}}$$

Definitions

$$f(\vec{r}) = \sum F_{\vec{k}}\, e^{+i\vec{k}\cdot\vec{r}} \qquad \frac{1}{\sqrt{V}}$$

$\boxed{3}$

$$\hat{V} \longrightarrow \sum_{\alpha,\beta} \int d^3r\, \hat{\psi}^{\dagger}_{\alpha}(\vec{r})\, \hat{V}(\vec{r})\, \hat{\psi}_{\beta}(\vec{r})$$

$$\hat{V} \rightarrow \sum_{\alpha,\beta} \int d^3r \; \psi_\alpha^*(\vec{r}) \; V(r) \; \psi_\beta(\vec{r})$$

$$= \sum_{\vec{k}_1, \vec{k}_2} \frac{1}{\mathcal{V}} \int d^3r \; e^{-i\vec{k}_1\cdot\vec{r}} \; \hat{V}(\vec{r}) \; e^{+i\vec{k}_2\cdot\vec{r}} \; \hat{c}^\dagger_{\vec{k}_1} \hat{c}_{\vec{k}_2}$$

$$= \sum_{\vec{k}_1, \vec{k}_2} \boxed{\frac{1}{\mathcal{V}} \int d^3r \; \boxed{\hat{V}(\vec{r})} \; \boxed{e^{-i(\vec{k}_1 - \vec{k}_2)\cdot\vec{r}}}} \; \hat{c}^\dagger_{\vec{k}_1} c_{\vec{k}_2}$$

$$= \sum_{\vec{k}_1, \vec{k}_2} \left(\mathcal{V}_{\vec{k}_1 - \vec{k}_2} \right) \hat{c}^\dagger_{\vec{k}_1} c_{\vec{k}_2}$$

Fourier coefficient at $\vec{k}_1 - \vec{k}_2$

Ex 3 Coulomb interaction $\hat{V}(\vec{r}_1, \vec{r}_2) = \hat{V}(\vec{r}_1 - \vec{r}_2)$

$$= \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

2nd quantized form

$r_1 - r_2$ $\quad r_2 - r_1$

$$\iint d^3r_1 \, d^3r_2 \; \hat{\psi}^\dagger_{\vec{k}}(\vec{r}_1) \; \hat{\psi}^\dagger_{\vec{k}'}(\vec{r}_2) \; \hat{V}(\vec{r}_1, \vec{r}_2) \; \hat{\psi}_{\vec{k}''}(\vec{r}_2) \; \hat{\psi}_{\vec{k}'''}(\vec{r}_1)$$

normal ordering

$$= \iint d^3r_1 \, d^3r_2 \; \frac{1}{\mathcal{V}^2} \sum_{\vec{k}, \vec{k}', \vec{k}'', \vec{k}'''} \hat{V}(\vec{r}_1, \vec{r}_2) \; e^{-i\vec{k}\cdot\vec{r}_1} \; e^{-i\vec{k}'\cdot\vec{r}_2} \; e^{+i\vec{k}''\cdot\vec{r}_2} \; e^{+i\vec{k}'''\cdot\vec{r}_1}$$

$$\underbrace{\hat{c}^\dagger_{\vec{k}} \; \hat{c}^\dagger_{\vec{k}'} \; \hat{c}_{\vec{k}''} \; \hat{c}_{\vec{k}'''}}$$

$$= \iint d^3r_1 \, d^3r_2 \frac{1}{\mathcal{V}^2} \sum_{\text{all } k'\text{s}} \hat{V}(\vec{r}_1, \vec{r}_2) \; \underbrace{e^{-i(\vec{k} - \vec{k}''')\cdot\vec{r}_1}} \; e^{-i(\vec{k}' - \vec{k}'')\cdot\vec{r}_2}$$

$\vec{z}$

$$= \iint d^3r_1\, d^3r_2 \frac{1}{V^2} \sum_{\text{all } \vec{k}'\text{s}} V(\vec{r}_1, \vec{r}_2)\, e \quad e$$

$$= \iint d^3r_1\, d^3r_2\, \frac{1}{V^2} \sum_{\text{all } k'\text{s}} \hat{V}(\underbrace{\vec{r}_1 - \vec{r}_2}_{\vec{z}})\, e^{-i(\vec{k}-\vec{k}''') \cdot \overbrace{(\vec{r}_1 - \vec{r}_2)}^{z}}\, e^{-i(\vec{k}-\vec{k}''')\cdot \vec{r}_2}\, e^{-i(\vec{k}'-\vec{k}'')\cdot \vec{r}_2} \times \hat{c}^\dagger_{\vec{k}}\, \hat{c}^\dagger_{\vec{k}'}\, \hat{c}_{\vec{k}''}\, \hat{c}_{\vec{k}'''}$$

$$= \iint d^3z\, d^3r_2\, \frac{1}{V^2} \sum_{\text{all } k'\text{s}} \hat{V}(\vec{z})\, e^{-i(\vec{k}-\vec{k}''')\cdot\vec{z}}\, e^{-i(\vec{k}-\vec{k}'''+\vec{k}'-\vec{k}'')\cdot\vec{r}_2}\, \hat{c}^\dagger_{\vec{k}}\, \hat{c}^\dagger_{\vec{k}'}\, \hat{c}_{\vec{k}''}\, \hat{c}_{\vec{k}'''}$$

$$= \int d^3r_2\, \frac{1}{V} \sum_{\text{all } k'\text{s}} \hat{v}_{\vec{k}-\vec{k}'''}\, e^{-i(\vec{k}-\vec{k}'''+\vec{k}'-\vec{k}'')\cdot\vec{r}_2}\, \hat{c}^\dagger_{\vec{k}}\, \hat{c}^\dagger_{\vec{k}'}\, \hat{c}_{\vec{k}''}\, \hat{c}_{\vec{k}'''}$$

$$= \sum_{\text{all } k'\text{s}} \hat{v}_{\vec{k}-\vec{k}'''} \left[\frac{1}{V} \int d^3r_2\, e^{-i(\vec{k}-\vec{k}'''+\vec{k}'-\vec{k}'')\cdot\vec{r}_2} \right] \hat{c}^\dagger_{\vec{k}}\, \hat{c}^\dagger_{\vec{k}'}\, \hat{c}_{\vec{k}''}\, \hat{c}_{\vec{k}'''}$$

$$= \sum_{\text{all } k'\text{s}} \hat{v}_{\underbrace{\vec{k}-(\vec{k}''+\vec{k}')}_{\vec{q}}}\, \delta_{\vec{k}''',\, \vec{k}+\vec{k}'-\vec{k}''}\, \hat{c}^\dagger_{\vec{k}}\, \hat{c}^\dagger_{\vec{k}'}\, \hat{c}_{\vec{k}''}\, \hat{c}_{\vec{k}'''}$$

$$\vec{k}'' \to \vec{p}_2 \qquad \vec{k}''' \to \vec{p}_1$$

$$= \sum_{\text{all } k'\text{s}} \hat{v}_{\vec{q}}\, \hat{c}^\dagger_{\vec{p}_1+\vec{q}}\, \hat{c}^\dagger_{\vec{p}_2-\vec{q}}\, \hat{c}_{\vec{k}''}\, \hat{c}_{\vec{k}+\vec{k}'-\vec{k}''}$$

check

Q.E.D.

$$\vec{k}'' - \vec{k}' = \vec{q}$$
$$\vec{k}' = \vec{k}'' - \vec{q} = \vec{p}_2 - \vec{q}$$

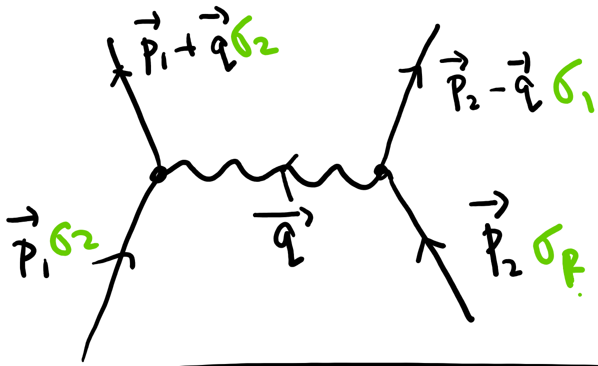
F.T.

$$\boxed{\hat{V}(\vec{r}_1 - \vec{r}_2) \xrightarrow{\text{becomes}} \sum_{\vec{p}_1, \vec{p}_2, \vec{q}} \boxed{\hat{v}_{\vec{q}}}\, \hat{c}^\dagger_{\vec{p}_1+\vec{q}}\, \hat{c}^\dagger_{\vec{p}_2-\vec{q}}\, \hat{c}_{\vec{p}_2}\, \hat{c}_{\vec{p}_1}}$$

$k' = k$ ...

$$\hat V(\vec r_1 - \vec r_2) \xrightarrow{\text{becomes}} \sum_{\vec p_1, \vec p_2, \vec q} \boxed{\tilde V_{\vec q}}\, \hat c^\dagger_{\vec p_1+\vec q}\, \hat c^\dagger_{\vec p_2-\vec q}\, \hat c_{\vec p_2}\, \hat c_{\vec p_1}$$

F.T.



Fourier transform for Coulombic repulsion

$$V(\vec r_1 - \vec r_2) = \left(\frac{e^2}{4\pi\varepsilon_0 |\vec r_1 - \vec r_2|} \right)$$

What's the F.T.

Let's start with

$$\boxed{\left(\sum_{\vec q}\right)} \frac{1}{q^2} e^{i\vec q\cdot\vec r}$$

integral

$$= \frac{V}{(2\pi)^3} \int d^3 q \,\frac{1}{q^2} e^{i\vec q\cdot\vec r}$$

$$= \frac{V}{(2\pi)^3} \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{q=0}^{\infty} d\phi\, d\theta\, dq\, \frac{\cancel{q^2}\sin\theta}{\cancel{q^2}} \cdot e^{iqr\cos\theta}$$

$\to z$

$iqr\cos\theta$

$$(2\pi)^3 \quad \phi=0 \quad \theta=0 \quad q=0 \qquad \cancel{q^2}$$

$$= \frac{V}{(2\pi)^3} (2\pi) \iint d\theta \, dq \; \sin\theta \; e^{iqr\cos\theta}$$

$$= \frac{V}{4\pi} \frac{1}{r} = \sum_{\vec{q}} \frac{1}{q^2} e^{i\vec{q}\cdot\vec{r}}$$

$$\checkmark \boxed{\frac{1}{r} = \left(\frac{4\pi}{V}\right) \sum_{\vec{q}} \frac{1}{q^2} e^{i\vec{q}\cdot\vec{r}}}$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} \qquad (\vec{r}_1 - \vec{r}_2) \;\;\underline{\underline{\;\;}}\;\; z.$$

$$f(r) = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r} = \boxed{\frac{e^2}{\varepsilon_0 V}} \boxed{\sum_{\vec{q}}} \boxed{\frac{1}{q^2}} e^{i\vec{q}\cdot\vec{r}}$$

$$\boxed{\hat{V}_{\vec{q}} = \left(\frac{e^2}{\varepsilon_0 V q^2}\right)} \longleftarrow \checkmark$$

F.T. of the Coulombic repulsion

$$H = \sum_l \frac{\hat{p}_l^2}{2m} + \sum_{\vec{r}_1, \vec{r}_2} \hat{V}(\vec{r}_1, \vec{r}_2) \cdots$$

$$\hat{H} = \sum_l \frac{\hat{p}_l^2}{2m} + \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0} \sum_{\substack{i,j \\ i \neq j}} \frac{1}{|\vec{r}_i - \vec{r}_j|}\right)$$

$\downarrow$ 2nd quantization form

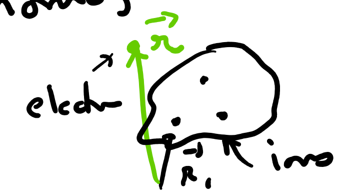
$$\boxed{\hat{H} = \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} + \frac{1}{2} \sum_{\vec{p}_1, \vec{p}_2, \vec{q}} \left(\frac{e^2}{\varepsilon_0 V q^2}\right) \hat{C}^{\dagger}_{\vec{p}_1+\vec{q}} \hat{C}^{\dagger}_{\vec{p}_2-\vec{q}} \hat{C}_{\vec{p}_2} \hat{C}_{\vec{p}_1}}$$

$$\vec{k} \quad 2m \quad 2 \sum_{\substack{\vec p_1, \vec p_2 \\ \vec q}} \left(\varepsilon_0 V q^2\right) \quad p_1 + q$$

Ions

Jellium

homogenous



$$\phi_{ions}(\vec{r}) = \int d^3r_1 \, \frac{e\, n(\vec{r}_1)}{4\pi\varepsilon_0 |\vec{r} - \vec{r}_1|}$$

$$\hat{H}_{electron-ion} = \frac{1}{2} \iint d^3r_1 \, d^3r \, \frac{(-e\, n(\vec{r}))\, e\, n(\vec{r}_1)}{4\pi\varepsilon_0 |\vec{r} - \vec{r}_1|}$$

$$= -\frac{e^2}{8\pi\varepsilon_0} \iint d^3r_1 \, d^3r \, \frac{n(\vec{r}_1)\, n(\vec{r})}{|\vec{r} - \vec{r}_1|}$$

$$= -\frac{e^2}{8\pi\varepsilon_0} \left(\frac{N}{V}\right)^2 \iint d^3r_1 \, d^3r \, \frac{1}{|\vec{r} - \vec{r}_1|}$$

$$= -\frac{e^2}{8\pi\varepsilon_0} \left(\frac{N}{V}\right)^2 \left(\frac{4\pi}{V}\right) \sum_{\vec q} \iint d^3r_1 \, d^3r \, \frac{1}{q^2} e^{+i\vec{q}\cdot(\vec{r} - \vec{r}_1)}$$

$$= -\frac{e^2}{8\pi\varepsilon_0} \left(\frac{N}{V}\right)^2 \left(\frac{4\pi}{V}\right) \sum_{\vec q} \frac{1}{q^2} \underbrace{\int d^3r_1 \, e^{-i\vec{q}\cdot\vec{r}_1}}_{V\delta_{\vec q, 0}} \underbrace{\int d^3r \, e^{+i\vec{q}\cdot\vec{r}}}_{V\delta_{\vec q \cdot 0}}$$

$$= -\frac{e^2 N^2}{\quad} \sum \frac{1}{\quad} \delta_{\vec{\ }}$$

$$= -\frac{e^2 N^2}{2\varepsilon_0 \mathcal{V}} \sum_{\vec{q}} \frac{1}{q^2}\, \delta_{\vec{q},0}$$

$$\hat{H} = \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} + \frac{1}{2} \sum_{\sigma_1 \sigma_2} \sum_{\vec{p}_1, \vec{p}_2, \vec{q}} \left(\frac{e^2}{\varepsilon_0 \mathcal{V} q^2}\right) \hat{c}^\dagger_{\vec{p}_1+\vec{q}\,\sigma_1} \hat{c}^\dagger_{\vec{p}_2-\vec{q}\,\sigma_2} \hat{c}_{\vec{p}_2\sigma_2} \hat{c}_{\vec{p}_1\sigma_1} - \frac{e^2 N^2}{2\varepsilon_0 \mathcal{V}} \sum_{\vec{q}} \frac{1}{q^2} \delta_{\vec{q},0}$$

$$\frac{1}{2} \sum_{\vec{p}_1, \vec{p}_2} \left(\frac{e^2}{\varepsilon_0 \mathcal{V} q^2}\right) \delta_{\vec{q},0}\, \hat{c}^\dagger_{\vec{p}_1} \hat{c}^\dagger_{\vec{p}_2} \hat{c}_{\vec{p}_2} \hat{c}_{\vec{p}_1}$$

$$= \frac{1}{2} \frac{e^2}{\varepsilon_0 \mathcal{V} q^2} \delta_{\vec{q},0} \underbrace{\left(\sum_{\vec{p}_1} \hat{c}^\dagger_{\vec{p}_1} c_{\vec{p}_1}\right)} \underbrace{\left(\sum_{\vec{p}_2} \hat{c}^\dagger_{\vec{p}_2} c_{\vec{p}_2}\right)}$$

$$= \frac{e^2 N^2}{2\varepsilon_0 \mathcal{V} q^2} \delta_{\vec{q},0}$$

$$\boxed{\hat{H} = \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} + \frac{1}{2} \sum_{\substack{\vec{p}_1, \vec{p}_2 \\ \vec{q} \neq 0}} \frac{e^2}{\varepsilon_0 \mathcal{V} q^2} \hat{c}^\dagger_{\vec{p}_1+\vec{q}\,\sigma_1} \hat{c}^\dagger_{\vec{p}_2-\vec{q}\,\sigma_2} \hat{c}_{\vec{p}_2\sigma_2} \hat{c}_{\vec{p}_1\sigma_1}}$$