2D UEG

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Abstract

A collection of notes on the 2D UEG. Note that for the 3D UEG, the only difference from the 2D case is the form of the Coulomb kernel in momentum space–instead of $V(\vec{q}) = 2\pi/q$ in 2D we have $V(\vec{q}) = 4\pi/q^2$ in 3D.

1 Bloch's theorem and the plane wave basis

In condensed matter physics, we are often interested in systems that obey periodic boundary conditions in a large volume Ω. We consider systems that comprise of repeating unit cells of volume Ω_{cell}, such that $\Omega = N_{\text{cell}}\Omega_{\text{cell}}$. Due to the translational symmetry in periodic systems, it is useful to employ a plane wave basis set in electronic structure calculations of such systems. In the coordinate representation, the basis functions are given by

$$\phi_i(\vec{r}) = \frac{1}{\sqrt{\Omega}}\, e^{i\vec{q}_i\cdot\vec{r}}, \tag{1}$$

where $\{\vec{q}_i\}$ are vectors in momentum space. By Bloch's theorem, we know that the eigenfunctions of the single-particle Schrödinger equation are of the form

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}), \tag{2}$$

where n labels the bands, and $\vec{k}$ is the crystal momentum restricted to the first Brillouin zone (BZ1). The functions $u_{n\vec{k}}(\vec{r})$ have the periodicity of the direct lattice, so we can Fourier expand them in terms of reciprocal lattice vectors:

$$u_{n\vec{k}}(\vec{r}) = \sum_i u_{n\vec{k},i}\; e^{i\vec{G}_i\cdot\vec{r}}, \tag{3}$$

where $u_{n\vec{k},\vec{G}}$ are the Fourier coefficients. Plugging this into (2), we have

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_i u_{n\vec{k},i}\; e^{i\vec{G}_i\cdot\vec{r}}. \tag{4}$$

This provides a rationale for us to *define* $\vec{q}_i = \vec{k} + \vec{G}_i$, so that the eigenfunctions $\psi_{n\vec{k}}$ can be directly expanded in the basis (with an additional $\vec{k}$ label):

$$\begin{aligned}
\psi_{n\vec{k}}(\vec{r}) &= e^{i\vec{k}\cdot\vec{r}} \sum_i u_{n\vec{k},i}\; e^{i\vec{G}_i\cdot\vec{r}} \\
&= \sum_i c_{n\vec{k},i} \left\{ \frac{1}{\sqrt{\Omega}}\; e^{i(\vec{k}+\vec{G}_i)\cdot\vec{r}} \right\} \qquad (5) \\
&= \sum_i c_{n\vec{k},i}\, \phi_{i\vec{k}}(\vec{r}). \qquad (6)
\end{aligned}$$

We normalize the eigenfunctions to unity in the volume Ω as follows:

$$\int_\Omega d^2\vec{r}\ \left[\psi_{m\vec{k}}(\vec{r})\right]^* \psi_{n\vec{k}'}(\vec{r}) = \delta_{mn}\delta_{\vec{k},\vec{k}'} \tag{7}$$

$$\begin{aligned}
\implies \int_\Omega d^2\vec{r}\ &\left\{\sum_i c_{m\vec{k},i}\ \phi_{i\vec{k}}(\vec{r})\right\}^* \left\{\sum_j c_{n\vec{k}',j}\ \phi_{j\vec{k}'}(\vec{r})\right\} \\
&= \sum_{ij} \left(c_{m\vec{k},i}\right)^* c_{n\vec{k}',j} \left\{\int_\Omega d^2\vec{r}\ \phi^*_{i\vec{k}}(\vec{r})\phi_{j\vec{k}'}(\vec{r})\right\} \\
&= \delta_{mn}\delta_{\vec{k},\vec{k}'}.
\end{aligned} \tag{8}$$

Usually we have $\sum_i \left(c_{m\vec{k},i}\right)^* c_{n\vec{k}',i} = \delta_{mn}\delta_{\vec{k},\vec{k}'}$, which implies

$$\int_\Omega d^2\vec{r}\ \phi^*_{i\vec{k}}(\vec{r})\phi_{j\vec{k}'}(\vec{r}) \propto \delta_{ij}. \tag{9}$$

Plugging in the basis functions, we have

$$\frac{1}{\Omega}\int_\Omega d^2\vec{r}\ e^{i\left[\vec{k}'-\vec{k}+\left(\vec{G}_j-\vec{G}_i\right)\right]\cdot\vec{r}} = \delta_{ij}\delta_{\vec{k},\vec{k}'}, \tag{10}$$

since $\vec{k},\vec{k}'$ are restricted to BZ1.

2 The density operator and its correlation functions[1]

Let us begin from field-theoretic formalism. The creation and annihilation *field operators* for spin-1/2 quantum fields are 2-component spinors, defined as

$$\hat{\Psi}^\dagger(\vec{r}) = \sum_p \begin{bmatrix}\psi_p^\uparrow(\vec{r})^*\ \hat{a}^\dagger_{p\uparrow} & \psi_p^\downarrow(\vec{r})^*\ \hat{a}^\dagger_{p\downarrow}\end{bmatrix} \tag{11}$$

$$\hat{\Psi}(\vec{r}) = \sum_p \begin{bmatrix}\psi_p^\uparrow(\vec{r})\ \hat{a}_{p\uparrow} \\ \psi_p^\downarrow(\vec{r})\ \hat{a}_{p\downarrow}\end{bmatrix}, \tag{12}$$

where $\psi_p^\sigma(\vec{r})$ is the spin σ-component of the single-particle wavefunction spinor $\vec{\psi}_p(\vec{r}) = [\psi_p^\uparrow(\vec{r})\ \psi_p^\downarrow(\vec{r})]^\mathsf{T}$ and $\hat{a}^\dagger_{p\sigma}(\hat{a}_{p\sigma})$ are creation (annihilation) operators for the state labelled by p with spin σ. Note that the sum is over the complete set of states p. The *density operator* at coordinate $\vec{r}$ is thus defined as

$$\begin{aligned}
\hat{n}(\vec{r}) = \hat{\Psi}^\dagger(\vec{r})\hat{\Psi}(\vec{r}) &= \sum_{pq} \begin{bmatrix}\psi_p^\uparrow(\vec{r})^*\ \hat{a}^\dagger_{p\uparrow} & \psi_p^\downarrow(\vec{r})^*\ \hat{a}^\dagger_{p\downarrow}\end{bmatrix} \begin{bmatrix}\psi_q^\uparrow(\vec{r})\ \hat{a}_{q\uparrow} \\ \psi_q^\downarrow(\vec{r})\ \hat{a}_{q\downarrow}\end{bmatrix} \\
&= \sum_{pq} \left[\psi_p^\uparrow(\vec{r})^*\psi_q^\uparrow(\vec{r})\ \hat{a}^\dagger_{p\uparrow}\hat{a}_{q\uparrow} + \psi_p^\downarrow(\vec{r})^*\psi_q^\downarrow(\vec{r})\ \hat{a}^\dagger_{p\downarrow}\hat{a}_{q\downarrow}\right] \\
&= \sum_\sigma\sum_{pq} \psi_p^\sigma(\vec{r})^*\psi_q^\sigma(\vec{r})\ \hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}.
\end{aligned} \tag{13}$$

[1] This section is adapted from Section 2.3 of [1].

Note that this is a one-body operator. A related quantity that is often considered in periodic systems is the *form factor*,

$$\hat{n}(\vec{q}) = \int d^d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\hat{n}(\vec{r}), \tag{14}$$

i.e. it is simply the Fourier transform of $\hat{n}(\vec{r})$.

Correlation functions of the density are averages of products of the density operator at different coordinates. An important instance is the *2-point density correlation function*:

$$\begin{aligned} C(\vec{r}_1,\vec{r}_2) &= \langle \hat{n}(\vec{r}_1)\hat{n}(\vec{r}_2)\rangle & (15)\\ &= \sum_{\sigma\tau}\sum_{pqrs}\psi_p^\sigma(\vec{r}_1)^*\psi_q^\sigma(\vec{r}_1)\psi_r^\tau(\vec{r}_2)^*\psi_s^\tau(\vec{r}_2)\,\langle \hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}\hat{a}^\dagger_{r\tau}\hat{a}_{s\tau}\rangle\,. & (16)\end{aligned}$$

Note that this is a two-body operator and we used the short-hand notation $\langle\hat{O}\rangle = \langle\Psi|\hat{O}|\Psi\rangle$ for some operator $\hat{O}$ and state $|\Psi\rangle$. The *structure function* is defined as the Fourier transform of the 2-point correlation function:

$$\begin{aligned} I(\vec{q}) &= \int d^d\vec{r}_1\; d^d\vec{r}_2\; e^{-i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)}C(\vec{r}_1,\vec{r}_2) \\ &= \int d^d\vec{r}_1\; d^d\vec{r}_2\; e^{-i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)}\,\langle \hat{n}(\vec{r}_1)\hat{n}(\vec{r}_2)\rangle \\ &= \langle \hat{n}(\vec{q})\hat{n}(-\vec{q})\rangle & (17)\\ &= \langle \hat{n}(\vec{q})\hat{n}^\dagger(\vec{q})\rangle\,. & (18)\end{aligned}$$

In the last line, we used

$$\hat{n}^\dagger(\vec{r}) = \left[\sum_\sigma\sum_{pq}\psi_p^\sigma(\vec{r})^*\psi_q^\sigma(\vec{r})\;\hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}\right]^\dagger = \sum_\sigma\sum_{qp}\psi_q^\sigma(\vec{r})^*\psi_p^\sigma(\vec{r})\;\hat{a}^\dagger_{q\sigma}\hat{a}_{p\sigma} = \hat{n}(\vec{r}) \tag{19}$$

$$\Longrightarrow\; \hat{n}(-\vec{q}) = \int d^d\vec{r}\; e^{i\vec{q}\cdot\vec{r}}\hat{n}(\vec{r}) = \left[\int d^d\vec{r}\; e^{-i\vec{q}\cdot\vec{r}}\hat{n}^\dagger(\vec{r})\right]^\dagger = \left[\int d^d\vec{r}\; e^{-i\vec{q}\cdot\vec{r}}\hat{n}(\vec{r})\right]^\dagger = \hat{n}^\dagger(\vec{q}). \tag{20}$$

Finally, the *static structure factor* is defined as[2]

$$S(\vec{q}) = \frac{1}{\Omega}I(\vec{q}), \tag{21}$$

where Ω is the volume of the system.

2.1 Slater determinant states

Let us specialize to a Slater determinant state $|\Psi\rangle$ constructed from the orbitals labelled by p. The average density $n(\vec{r})$ (i.e. the electron density) is

$$\begin{aligned} n(\vec{r}) = \langle\Psi|\hat{n}(\vec{r})|\Psi\rangle &= \sum_\sigma\sum_{pq}\psi_p^\sigma(\vec{r})^*\psi_q^\sigma(\vec{r})\,\langle\Psi|\hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}|\Psi\rangle \\ &= \sum_\sigma\sum_{pq,\mathrm{occ}}\psi_p^\sigma(\vec{r})^*\psi_q^\sigma(\vec{r})\delta_{pq} \\ &= \sum_\sigma\sum_{p,\mathrm{occ}}\left|\psi_p^\sigma(\vec{r})\right|^2, & (22)\end{aligned}$$

[2] While (21) is more often used for quantum fluids, the definition $S(\vec{q}) = \frac{1}{N}I(\vec{q})$ is more commonly used for classical fluids.

which is the familiar density function in the coordinate representation. The average form factor is

$$n(\vec{q}) = \int d^d\vec{r}\; e^{-i\vec{q}\cdot\vec{r}} n(\vec{r}). \tag{23}$$

The 2-point density correlation function is given by[3]

$$\begin{aligned}
C(\vec{r}_1,\vec{r}_2) &= \langle\Psi|\hat{n}(\vec{r}_1)\hat{n}(\vec{r}_2)|\Psi\rangle \\
&= \sum_{\sigma\sigma'}\sum_{pqrs} \psi_p^\sigma(\vec{r}_1)^*\psi_q^\sigma(\vec{r}_1)\psi_r^{\sigma'}(\vec{r}_2)^*\psi_s^{\sigma'}(\vec{r}_2)\,\langle\Psi|\hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}\hat{a}^\dagger_{r\sigma'}\hat{a}_{s\sigma'}|\Psi\rangle \\
&= \sum_{\sigma\sigma'}\sum_{pqrs} \psi_p^\sigma(\vec{r}_1)^*\psi_q^\sigma(\vec{r}_1)\psi_r^{\sigma'}(\vec{r}_2)^*\psi_s^{\sigma'}(\vec{r}_2)\,[\delta_{pq,\mathrm{occ}}\;\delta_{rs,\mathrm{occ}} - \delta_{\sigma\sigma'}\delta_{ps,\mathrm{occ}}\;\delta_{qr,\mathrm{occ}} + \delta_{\sigma\sigma'}\delta_{ps,\mathrm{occ}}\;\delta_{qr}] \\
&= \sum_{\sigma\sigma'}\sum_{pr,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^*\psi_p^\sigma(\vec{r}_1)\psi_r^{\sigma'}(\vec{r}_2)^*\psi_r^{\sigma'}(\vec{r}_2) - \sum_{\sigma}\sum_{pq,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^*\psi_q^\sigma(\vec{r}_1)\psi_q^\sigma(\vec{r}_2)^*\psi_p^\sigma(\vec{r}_2) \\
&\quad + \sum_{\sigma}\sum_{p,\mathrm{occ}}\sum_{q} \psi_p^\sigma(\vec{r}_1)^*\psi_q^\sigma(\vec{r}_1)\psi_q^\sigma(\vec{r}_2)^*\psi_p^\sigma(\vec{r}_2) \\
&= \left[\sum_{\sigma}\sum_{p,\mathrm{occ}} \left|\psi_p^\sigma(\vec{r}_1)\right|^2\right]\left[\sum_{\sigma'}\sum_{r,\mathrm{occ}} \left|\psi_r^{\sigma'}(\vec{r}_2)\right|^2\right] - \sum_{\sigma}\left[\sum_{p,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^*\psi_p^\sigma(\vec{r}_2)\right]\left[\sum_{q,\mathrm{occ}} \psi_q^\sigma(\vec{r}_2)^*\psi_q^\sigma(\vec{r}_1)\right] \\
&\quad + \left[\sum_{q} \psi_q^\sigma(\vec{r}_2)^*\psi_q^\sigma(\vec{r}_1)\right]\left[\sum_{\sigma}\sum_{p,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^*\psi_p^\sigma(\vec{r}_2)\right] \\
&= n(\vec{r}_1)n(\vec{r}_2) - n(\vec{r}_1,\vec{r}_2)n(\vec{r}_2,\vec{r}_1) + \delta(\vec{r}_1-\vec{r}_2)n(\vec{r}_1,\vec{r}_2),
\end{aligned} \tag{24}$$

where we write more generally,

$$\hat{n}(\vec{r}_1,\vec{r}_2) = \hat{\Psi}^\dagger(\vec{r}_1)\hat{\Psi}(\vec{r}_2) = \sum_{\sigma}\sum_{pq} \psi_p^\sigma(\vec{r}_1)^*\psi_q^\sigma(\vec{r}_2)\;\hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma} \tag{25}$$

$$\implies n(\vec{r}_1,\vec{r}_2) = \langle\Psi|\hat{n}(\vec{r}_1,\vec{r}_2)|\Psi\rangle = \sum_{\sigma}\sum_{p,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^*\psi_p^\sigma(\vec{r}_2) \tag{26}$$

$$n(\vec{r}_1) = n(\vec{r}_1,\vec{r}_1). \tag{27}$$

Notice that

$$n(\vec{r}_2,\vec{r}_1) = \sum_{\sigma}\sum_{p,\mathrm{occ}} \psi_p^\sigma(\vec{r}_2)^*\psi_p^\sigma(\vec{r}_1) = \left[\sum_{\sigma}\sum_{p,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^*\psi_p^\sigma(\vec{r}_2)\right]^* = n(\vec{r}_1,\vec{r}_2)^*. \tag{28}$$

Thus, we have for the 2-point density correlation function:

$$C(\vec{r}_1,\vec{r}_2) = n(\vec{r}_1)n(\vec{r}_2) - |n(\vec{r}_1,\vec{r}_2)|^2 + \delta(\vec{r}_1-\vec{r}_2)n(\vec{r}_1,\vec{r}_2). \tag{29}$$

[3] We used

$$\begin{aligned}
\langle\Psi|\hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}\hat{a}^\dagger_{r\sigma'}\hat{a}_{s\sigma'}|\Psi\rangle &= \langle\hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}\rangle\,\langle\hat{a}^\dagger_{r\sigma'}\hat{a}_{s\sigma'}\rangle - \cancel{\langle\hat{a}^\dagger_{p\sigma}\hat{a}^\dagger_{r\sigma'}\rangle\,\langle\hat{a}_{q\sigma}\hat{a}_{s\sigma'}\rangle} + \langle\hat{a}^\dagger_{p\sigma}\hat{a}_{s\sigma'}\rangle\,\langle\hat{a}_{q\sigma}\hat{a}^\dagger_{r\sigma'}\rangle \quad \text{(Wick's theorem)} \\
&= \langle\hat{a}^\dagger_{p\sigma}\hat{a}_{q\sigma}\rangle\,\langle\hat{a}^\dagger_{r\sigma'}\hat{a}_{s\sigma'}\rangle + \langle\hat{a}^\dagger_{p\sigma}\hat{a}_{s\sigma'}\rangle\left[\delta_{qr}\delta_{\sigma\sigma'} - \langle\hat{a}^\dagger_{r\sigma'}\hat{a}_{q\sigma}\rangle\right] \\
&= \delta_{pq,\mathrm{occ}}\cdot\delta_{rs,\mathrm{occ}} + \delta_{ps,\mathrm{occ}}\;\delta_{\sigma\sigma'}\cdot\delta_{qr}\;\delta_{\sigma\sigma'} - \delta_{ps,\mathrm{occ}}\;\delta_{\sigma\sigma'}\cdot\delta_{qr,\mathrm{occ}}\;\delta_{\sigma\sigma'} \\
&= \delta_{pq,\mathrm{occ}}\;\delta_{rs,\mathrm{occ}} - \delta_{\sigma\sigma'}\delta_{ps,\mathrm{occ}}\;\delta_{qr,\mathrm{occ}} + \delta_{\sigma\sigma'}\delta_{ps,\mathrm{occ}}\;\delta_{qr},
\end{aligned}$$

where $\langle\cdots\rangle$ is shorthand for $\langle\Psi|\cdots|\Psi\rangle$.

For the special case $\vec{r}_1 = \vec{r}_2$,

$$C(\vec{r}_1, \vec{r}_1) = n(\vec{r}_1)^2 - n(\vec{r}_1)^2 + \delta(0) n(\vec{r}_1) = \delta(0) n(\vec{r}_1), \tag{30}$$

i.e. we should see a sharp peak.

Finally, the static structure factor is:

$$\begin{aligned}
S(\vec{q}) &= \frac{1}{\Omega} \int d^d\vec{r}_1 \; d^d\vec{r}_2 \; e^{-i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} C(\vec{r}_1, \vec{r}_2) \\
&= \frac{1}{\Omega} \int d^d\vec{r}_1 \; d^d\vec{r}_2 \; e^{-i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} \left[\underbrace{n(\vec{r}_1) n(\vec{r}_2)}_{1} - \underbrace{|n(\vec{r}_1, \vec{r}_2)|^2}_{2} + \underbrace{\delta(\vec{r}_1 - \vec{r}_2) n(\vec{r}_1, \vec{r}_2)}_{3} \right] \\
3 &= \int d^d\vec{r}_1 \; d^d\vec{r}_2 \; e^{-i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} \delta(\vec{r}_1 - \vec{r}_2) n(\vec{r}_1, \vec{r}_2) \\
&= \int d^d\vec{r}_1 \; n(\vec{r}_1, \vec{r}_1) \\
&= N && (31) \\
1 &= \int d^d\vec{r}_1 \; e^{-i\vec{q}\cdot\vec{r}_1} n(\vec{r}_1) \int d^d\vec{r}_2 \; e^{i\vec{q}\cdot\vec{r}_2} n(\vec{r}_2) \\
&= \int d^d\vec{r}_1 \; e^{-i\vec{q}\cdot\vec{r}_1} n(\vec{r}_1) \left[\int d^d\vec{r}_2 \; e^{-i\vec{q}\cdot\vec{r}_2} n(\vec{r}_2) \right]^* \\
&= |n(\vec{q})|^2 && (32) \\
2 &= \int d^d\vec{r}_1 \; d^d\vec{r}_2 \; e^{-i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} n(\vec{r}_1, \vec{r}_2) n(\vec{r}_1, \vec{r}_2)^* \\
&= \int d^d\vec{r}_1 \; d^d\vec{r}_2 \; e^{-i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} \left[\sum_{\sigma} \sum_{p,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^* \psi_p^\sigma(\vec{r}_2) \right] \left[\sum_{\sigma'} \sum_{s,\mathrm{occ}} \psi_s^{\sigma'}(\vec{r}_1)^* \psi_s^{\sigma'}(\vec{r}_2) \right]^* \\
&= \sum_{\sigma\sigma'} \sum_{ps,\mathrm{occ}} \int d^d\vec{r}_1 \; d^d\vec{r}_2 \; e^{-i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} \left[\psi_p^\sigma(\vec{r}_1)^* \psi_s^{\sigma'}(\vec{r}_1) \right] \left[\psi_s^{\sigma'}(\vec{r}_2)^* \psi_p^\sigma(\vec{r}_2) \right]. && (33)
\end{aligned}$$

Expanding ψ_p^σ in the plane wave basis functions (1),

$$
\begin{aligned}
n(\vec{q}) = \int d^d\vec{r}_1\ e^{-i\vec{q}\cdot\vec{r}_1} n(\vec{r}_1) &= \int d^d\vec{r}_1\ e^{-i\vec{q}\cdot\vec{r}_1} \left[\sum_\sigma \sum_{p,\mathrm{occ}} \psi_p^\sigma(\vec{r}_1)^* \psi_p^\sigma(\vec{r}_1)\right] \\
&= \sum_\sigma \sum_{p,\mathrm{occ}} \int d^d\vec{r}_1\ e^{-i\vec{q}\cdot\vec{r}_1} \left[\sum_i \left(c_{ip}^\sigma\right)^* \phi_i(\vec{r}_1)^*\right] \left[\sum_j c_{jp}^\sigma \phi_j(\vec{r}_1)\right] \\
&= \sum_{ij} \sum_\sigma \sum_{p,\mathrm{occ}} \left(c_{ip}^\sigma\right)^* c_{jp}^\sigma \int d^d\vec{r}_1\ e^{-i\vec{q}\cdot\vec{r}_1} \phi_i(\vec{r}_1)^* \phi_j(\vec{r}_1) \\
&= \sum_{ij} \left[\sum_\sigma \sum_{p,\mathrm{occ}} \left(c_{ip}^\sigma\right)^* c_{jp}^\sigma\right] \cdot \frac{1}{\Omega} \int d^d\vec{r}_1\ e^{-i\vec{q}\cdot\vec{r}_1} e^{-i\vec{G}_i\cdot\vec{r}_1} e^{i\vec{G}_j\cdot\vec{r}_1} \\
&= \sum_{ij} \left[\sum_\sigma P_{ji}^\sigma\right] \cdot \frac{1}{\Omega} \int d^d\vec{r}_1\ e^{i(\vec{G}_j - \vec{G}_i - \vec{q})\cdot\vec{r}_1} \\
&= \sum_{ij} \left[\sum_\sigma P_{ji}^\sigma\right] \cdot \frac{1}{\Omega} \cdot \Omega\ \delta_{j,i+q} \quad (\vec{q} \in \{\vec{G}_i\},\ \text{else we get } 0) \\
&= \sum_i \left[\sum_\sigma P_{i+q,i}^\sigma\right].
\end{aligned} \tag{34}
$$

$$
\implies 1 = \sum_{ij} \left[\sum_\sigma \left(P_{i+q,i}^\sigma\right)^*\right] \left[\sum_{\sigma'} P_{j+q,j}^{\sigma'}\right]. \tag{35}
$$

$$
\begin{aligned}
2 &= \sum_{\sigma\sigma'} \sum_{ps,\mathrm{occ}} \int d^d\vec{r}_1\ d^d\vec{r}_2\ e^{-i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)} \left[\sum_i \left(c_{ip}^\sigma\right)^* \phi_i(\vec{r}_1)^*\right] \left[\sum_j c_{js}^{\sigma'} \phi_j(\vec{r}_1)\right] \left[\sum_k \left(c_{ks}^{\sigma'}\right)^* \phi_k(\vec{r}_2)^*\right] \left[\sum_l c_{lp}^\sigma \phi_l(\vec{r}_2)\right] \\
&= \sum_{ijkl} \sum_{\sigma\sigma'} \sum_{ps,\mathrm{occ}} \left(c_{ip}^\sigma\right)^* c_{lp}^\sigma \left(c_{ks}^{\sigma'}\right)^* c_{js}^{\sigma'} \int d^d\vec{r}_1\ d^d\vec{r}_2\ e^{-i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)} \left[\phi_i(\vec{r}_1)^* \phi_j(\vec{r}_1)\right] \left[\phi_k(\vec{r}_2)^* \phi_l(\vec{r}_2)\right] \\
&= \sum_{ijkl} \left[\sum_\sigma \sum_{p,\mathrm{occ}} \left(c_{ip}^\sigma\right)^* c_{lp}^\sigma\right] \left[\sum_{\sigma'} \sum_{s,\mathrm{occ}} \left(c_{ks}^{\sigma'}\right)^* c_{js}^{\sigma'}\right] \cdot \frac{1}{\Omega^2} \int d^d\vec{r}_1\ e^{-i\vec{q}\cdot\vec{r}_1} e^{-i\vec{G}_i\cdot\vec{r}_1} e^{i\vec{G}_j\cdot\vec{r}_1} \int d^d\vec{r}_2\ e^{i\vec{q}\cdot\vec{r}_2} e^{-i\vec{G}_k\cdot\vec{r}_1} e^{i\vec{G}_l\cdot\vec{r}_1} \\
&= \sum_{ijkl} \left[\sum_\sigma P_{li}^\sigma\right] \left[\sum_{\sigma'} P_{jk}^{\sigma'}\right] \cdot \frac{1}{\Omega^2} \int d^d\vec{r}_1\ e^{i(\vec{G}_j - \vec{G}_i - \vec{q})\cdot\vec{r}_1} \int d^d\vec{r}_2\ e^{i(\vec{G}_l - \vec{G}_k + \vec{q})\cdot\vec{r}_2} \\
&= \sum_{ijkl} \left[\sum_\sigma P_{li}^\sigma\right] \left[\sum_{\sigma'} P_{jk}^{\sigma'}\right] \cdot \frac{1}{\Omega^2} \cdot \Omega\ \delta_{j,i+q} \cdot \Omega\ \delta_{l,k-q} \quad (\vec{q} \in \{\vec{G}_i\},\ \text{else we get } 0) \\
&= \sum_{ik} \left[\sum_\sigma P_{k-q,i}^\sigma\right] \left[\sum_{\sigma'} P_{i+q,k}^{\sigma'}\right] \\
&= \sum_{ik} \left[\sum_\sigma \left(P_{i,k-q}^\sigma\right)^*\right] \left[\sum_{\sigma'} P_{i+q,k}^{\sigma'}\right] \\
&= \sum_{ij} \left[\sum_\sigma \left(P_{ij}^\sigma\right)^*\right] \left[\sum_{\sigma'} P_{i+q,j+q}^{\sigma'}\right] \quad (j = k - q),
\end{aligned} \tag{36}
$$

where $\mathbf{P}^\sigma = \mathbf{C}^\sigma \left(\mathbf{C}^\sigma\right)^\dagger$ is the σ-spin density matrix in the plane wave basis. Putting it all together:

$$S(\vec{q} \in \{\vec{G}_i\}) = \frac{1}{\Omega}\left\{ |n(\vec{q})|^2 - \sum_{ij}\left[\sum_\sigma \left(P^\sigma_{ij}\right)^*\right]\left[\sum_{\sigma'} P^{\sigma'}_{i+q,j+q}\right] + N \right\} \tag{37}$$

$$= \frac{1}{\Omega}\left\{ \sum_{ij}\left[\sum_\sigma \left(P^\sigma_{i+q,i}\right)^*\right]\left[\sum_{\sigma'} P^{\sigma'}_{j+q,j}\right] - \sum_{ij}\left[\sum_\sigma \left(P^\sigma_{ij}\right)^*\right]\left[\sum_{\sigma'} P^{\sigma'}_{i+q,j+q}\right] + N \right\} \tag{38}$$

$$S(\vec{q} \notin \{\vec{G}_i\}) = \frac{N}{\Omega}. \tag{39}$$

We can calculate $|n(\vec{q})|^2$ using the Fast Fourier Transform (see **??** for details).

2.2 The electron density

2.2.1 Spin-unrestricted formalism

In the spin-unrestricted formalism, we assume that the single-particle wavefunction spinors $\vec{\psi}_{n\vec{k}}(\vec{r})$ are spin-polarized, i.e. they are of the form

$$\vec{\psi}_{n\vec{k}}(\vec{r}) = \begin{bmatrix} \psi^\uparrow_{n\vec{k}}(\vec{r}) \\ 0 \end{bmatrix}, \quad \vec{\psi}_{m\vec{k}'}(\vec{r}) = \begin{bmatrix} 0 \\ \psi^\downarrow_{m\vec{k}'}(\vec{r}) \end{bmatrix}, \quad (n,\vec{k}) \neq (m,\vec{k}'). \tag{40}$$

This simplification allows us to work directly with $\psi^\sigma_{n\vec{k}}$. Expanding in the set of basis functions $\{\phi_{i\vec{k}}\}$ which we assume to not carry spin labels, we have

$$\psi^\sigma_{n\vec{k}}(\vec{r}) = \sum_i c^\sigma_{n\vec{k},i}\phi_{i\vec{k}}(\vec{r}). \tag{41}$$

From (22), the electron density at some point $\vec{r} \in \Omega$ is

$$n(\vec{r}) = \sum_\sigma \left\{ \sum_{n,\mathrm{occ}} \sum_{\vec{k}} |\psi^\sigma_{n\vec{k}}(\vec{r})|^2 \right\} = \sum_{\vec{k}} n_{\vec{k}}(\vec{r}) \tag{42}$$

$$n_{\vec{k}}(\vec{r}) = \sum_\sigma \sum_{n,\mathrm{occ}} |\psi^\sigma_{n\vec{k}}(\vec{r})|^2. \tag{43}$$

In the thermodynamic limit $\Omega \to \infty$ such that the density $n = N/\Omega$ is kept constant, the sums are replaced with integrals:

$$\sum_{\vec{k}} \to \frac{\Omega}{(2\pi)^2}\int_{\mathrm{BZ}} d^2\vec{k} \tag{44}$$

$$\implies n(\vec{r}) = \sum_{\vec{k}} n_{\vec{k}}(\vec{r}) = \frac{\Omega}{(2\pi)^2}\int_{\mathrm{BZ}} d^2\vec{k}\,\left\{ \sum_\sigma \sum_{n,\mathrm{occ}} |\psi^\sigma_{n\vec{k}}(\vec{r})|^2 \right\}. \tag{45}$$

In practice, the integral is computed using schemes that involve $\vec{k}$-point sampling, where a weighted sum over $\vec{k}$ is employed:

$$n(\vec{r}) \approx \sum_{\vec{k}} w_{\vec{k}} n_{\vec{k}}(\vec{r}). \tag{46}$$

The weight $\omega_{\vec{k}}$ is typically $1/N_{\vec{k}}$, where $N_{\vec{k}}$ is the number of $\vec{k}$-points, *i.e.* (46) is simply the charge density averaged over $\vec{k}$-points. Explicitly writing out $n(\vec{r})$ in the plane wave basis $\{\phi_{i\vec{k}}\}$, we have

$$\begin{aligned} n(\vec{r}) &\approx \frac{1}{N_{\vec{k}}}\sum_{\vec{k}}\left\{\sum_{\sigma}\sum_{n,\mathrm{occ}}\left[\sum_{i} c^{\sigma}_{n\vec{k},i}\ \phi_{i\vec{k}}(\vec{r})\right]^{*}\left[\sum_{j} c^{\sigma}_{n\vec{k},j}\ \phi_{j\vec{k}}(\vec{r})\right]\right\} \\ &= \frac{1}{N_{\vec{k}}}\sum_{\vec{k}\sigma}\sum_{ij}\phi^{*}_{i\vec{k}}(\vec{r})\phi_{j\vec{k}}(\vec{r})\left\{\sum_{n,\mathrm{occ}} c^{\sigma}_{n\vec{k},j}\left(c^{\sigma}_{n\vec{k},i}\right)^{*}\right\} \\ &= \frac{1}{N_{\vec{k}}}\sum_{\vec{k}\sigma}\sum_{ij}\phi^{*}_{i\vec{k}}(\vec{r})\phi_{j\vec{k}}(\vec{r})P^{\sigma}_{\vec{k},ji}, \end{aligned} \tag{47}$$

where $\mathbf{P}^{\sigma}_{\vec{k}} = \mathbf{C}^{\sigma}_{\vec{k}}\left(\mathbf{C}^{\sigma}_{\vec{k}}\right)^{\dagger}$ is the σ-spin density matrix at $\vec{k} \in$ BZ1 in the plane wave basis. We can also evaluate the Fourier transform of $n(\vec{r})$:

$$n(\vec{r}) = \sum_{m} n_m\ e^{i\vec{G}_m\cdot\vec{r}} \tag{48}$$

$$\begin{aligned} \implies\ n_m &= \int_{\Omega} d^2\vec{r}\ n(\vec{r})\ e^{-i\vec{G}_m\cdot\vec{r}} \\ &= \int_{\Omega} d^2\vec{r}\left\{\frac{1}{N_{\vec{k}}}\sum_{\vec{k}\sigma}\sum_{ij}\phi^{*}_{i\vec{k}}(\vec{r})\phi_{j\vec{k}}(\vec{r})P^{\sigma}_{\vec{k},ji}\right\} e^{-i\vec{G}_m\cdot\vec{r}} \\ &= \frac{1}{N_{\vec{k}}}\sum_{\vec{k}\sigma}\sum_{ij}P^{\sigma}_{\vec{k},ji}\cdot\frac{1}{\Omega}\int_{\Omega} d^2\vec{r}\ e^{-i(\vec{G}_i-\vec{G}_j+\vec{G}_m)\cdot\vec{r}} \\ &= \frac{1}{N_{\vec{k}}}\sum_{\vec{k}\sigma}\sum_{ij}P^{\sigma}_{\vec{k},ji}\cdot\frac{1}{\Omega}\cdot\Omega\ \delta_{i,j-m} \\ &= \frac{1}{N_{\vec{k}}}\sum_{\vec{k}\sigma}\sum_{j}P^{\sigma}_{\vec{k},j,j-m}. \end{aligned} \tag{49}$$

2.2.2 Spin-generalized formalism

In the spin-generalized formalism, we retain the spinor structure of the wavefunction which allows the orbitals to exhibit both spin up and down character. Expanding in the same spinless basis functions $\{\phi_{i\vec{k}}\}$, we have

$$\vec{\psi}_{n\vec{k}}(\vec{r}) = \begin{bmatrix}\psi^{\uparrow}_{n\vec{k}}(\vec{r}) \\ \psi^{\downarrow}_{n\vec{k}}(\vec{r})\end{bmatrix} = \begin{bmatrix}\sum_i c^{\uparrow}_{n\vec{k},i}\phi_{i\vec{k}}(\vec{r}) \\ \sum_i c^{\downarrow}_{n\vec{k},i}\phi_{i\vec{k}}(\vec{r})\end{bmatrix}. \tag{50}$$

The electron density, obtained from (22), (43), (47), is similar to the spin-unrestricted formalism:

$$n(\vec{r}) = \sum_{\sigma}\sum_{n,\mathrm{occ}}\sum_{\vec{k}}|\psi^{\sigma}_{n\vec{k}}(\vec{r})|^2 \approx \frac{1}{N_{\vec{k}}}\sum_{\vec{k}\sigma}\sum_{ij}\phi^{*}_{i\vec{k}}(\vec{r})\phi_{j\vec{k}}(\vec{r})P^{\sigma\sigma}_{\vec{k},ji}. \tag{51}$$

In the generalized formalism, note that the density matrix $\mathbf{P}_{\vec{k}}$ is a block matrix constructed from the submatrices $\mathbf{P}_{\vec{k}}^{\sigma\sigma'}$:

$$\mathbf{P}_{\vec{k}} = \begin{bmatrix} \mathbf{P}_{\vec{k}}^{\uparrow\uparrow} & \mathbf{P}_{\vec{k}}^{\uparrow\downarrow} \\ \mathbf{P}_{\vec{k}}^{\downarrow\uparrow} & \mathbf{P}_{\vec{k}}^{\downarrow\downarrow} \end{bmatrix} \tag{52}$$

$$\mathbf{P}_{\vec{k}}^{\sigma\sigma'} = \mathbf{C}_{\vec{k}}^{\sigma} \left(\mathbf{C}_{\vec{k}}^{\sigma'}\right)^{\dagger}. \tag{53}$$

If there are M basis functions, the generalized coefficient matrices $\mathbf{C}_{\vec{k}}$ have dimension $2M \times M$ and are of the form

$$\mathbf{C}_{\vec{k}} = \begin{bmatrix} \mathbf{C}_{\vec{k}}^{\uparrow} \\ \mathbf{C}_{\vec{k}}^{\downarrow} \end{bmatrix}. \tag{54}$$

3 Hartree-Fock theory

Recall that in the usual Hartree-Fock (HF) theory for molecular systems, the true wavefunction is approximated with a single Slater determinant:

$$|\Psi_{\mathrm{HF}}\rangle = |\chi_i(\vec{x}_1)\chi_j(\vec{x}_2)\ldots\rangle\,, \tag{55}$$

where χ_i are molecular orbitals (MOs) and $\vec{x} = (\vec{r}, \omega)$ denotes the composite spatial and spin coordinates. Variationally minimizing $E_{\mathrm{HF}} = \langle\Psi_{\mathrm{HF}}|\hat{H}|\Psi_{\mathrm{HF}}\rangle$, we obtain the canonical HF equations:

$$\hat{F}\,|\chi_i\rangle = \epsilon_i\,|\chi_i\rangle\,, \tag{56}$$

where $\hat{F}$ is the single-particle Fock operator. In 1st-quantized form,

$$\begin{aligned} \hat{F}(\vec{x})\chi_i(\vec{x}) &= \left[\hat{T}(\vec{x}) + \hat{J}(\vec{x}) - \hat{K}(\vec{x})\right]\chi_i(\vec{x}) \\ &= -\frac{1}{2}\nabla_{\vec{r}}^2\chi_i(\vec{x}) + \left\{\sum_j \int dx'\ \frac{\chi_j^*\left(x'\right)\chi_j\left(\vec{x'}\right)}{|\vec{r}-\vec{r'}|}\right\}\chi_i(\vec{x}) - \left\{\sum_j \int d\vec{x'}\ \frac{\chi_j^*\left(\vec{x'}\right)\chi_i\left(\vec{x'}\right)}{|\vec{r}-\vec{r'}|}\right\}\chi_j(\vec{x}). \end{aligned} \tag{57}$$

3.1 Unrestricted HF

3.1.1 Plane wave basis

In periodic systems where there exists a periodic potential, the MOs are Bloch orbitals of the form

$$\chi_i^{\sigma}(\vec{r}) \longrightarrow \psi_{n\vec{k}}^{\sigma}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}^{\sigma}(\vec{r}), \tag{58}$$

where σ labels the spin, $\vec{k}$ is the crystal momentum quantum number, n is the band index, and $u_{n\vec{k}}^{\sigma}$ is a function with the periodicity of the direct lattice. As discussed in 1, we can further expand

$$\psi_{n\vec{k}}^{\sigma}(\vec{r}) = \sum_i c_{n\vec{k},i}^{\sigma}\phi_{\vec{k}i}(\vec{r}) = \sum_i \underbrace{c_{n\vec{k},i}^{\sigma}}_{\substack{\text{MO}\\ \text{coefficient}}}\ \underbrace{e^{i\vec{k}\cdot\vec{r}}\phi_i(\vec{r})}_{\text{AO}}. \tag{59}$$

3.1.2 The Coulomb potential, $J^{\sigma}_{\vec{k}}(\vec{r})$

From Eq 3.319 in [2], the Coulomb potential is defined as

$$J^{\sigma}_{n\vec{k}}(\vec{r}) = \int d^2\vec{r'}\ \psi^{\sigma*}_{n\vec{k}}(\vec{r'}) \frac{1}{|\vec{r}-\vec{r'}|} \psi^{\sigma}_{n\vec{k}}(\vec{r'}) \tag{60}$$

$$J^{\sigma}(\vec{r}) = \sum_{\vec{k}} \sum_{n,\mathrm{occ}} J^{\sigma}_{n\vec{k}}(\vec{r}). \qquad \text{(total Coulomb potential)} \tag{61}$$

In the plane wave basis, we have

$$\begin{aligned} J^{\sigma}_{\vec{k},pq} &= \int_{\Omega} d^2\vec{r}\ \phi^{*}_{p\vec{k}}(\vec{r}) J^{\sigma}(\vec{r}) \phi_{q\vec{k}}(\vec{r}) \\ &= \int_{\Omega} d^2\vec{r}\ \phi^{*}_{p\vec{k}}(\vec{r}) \sum_{\vec{k'}} \sum_{n,\mathrm{occ}} \left[\int d^2\vec{r'}\ \psi^{\sigma*}_{n\vec{k'}}(\vec{r'}) \frac{1}{|\vec{r}-\vec{r'}|} \psi^{\sigma}_{n\vec{k'}}(\vec{r'}) \right] \phi_{q\vec{k}}(\vec{r}). \end{aligned} \tag{62}$$

Expanding $\psi^{\sigma}_{n\vec{k'}}(\vec{r}) = \sum_i c^{\sigma}_{n\vec{k'},i} \phi_{i\vec{k'}}(\vec{r})$,

$$\begin{aligned} J^{\sigma}_{\vec{k},pq} &= \sum_{\vec{k'}} \sum_{n,\mathrm{occ}} \int_{\Omega} d^2\vec{r} \int d^2\vec{r'}\ \phi^{*}_{p\vec{k}}(\vec{r}) \left\{ \sum_i c^{\sigma}_{n\vec{k'},i} \phi_{i\vec{k'}}(\vec{r'}) \right\}^{*} \frac{1}{|\vec{r}-\vec{r'}|} \left\{ \sum_j c^{\sigma}_{n\vec{k'},j} \phi_{j\vec{k'}}(\vec{r'}) \right\} \phi_{q\vec{k}}(\vec{r}) \\ &= \sum_{ij} \left[\sum_{\vec{k'}} \sum_{n,\mathrm{occ}} c^{\sigma}_{n\vec{k'},j} \left(c^{\sigma}_{n\vec{k'},i} \right)^{*} \right] \left[\int_{\Omega} d^2\vec{r} \int d^2\vec{r'}\ \phi^{*}_{p\vec{k}}(\vec{r}) \phi^{*}_{i\vec{k'}}(\vec{r'}) \frac{1}{|\vec{r}-\vec{r'}|} \phi_{q\vec{k}}(\vec{r}) \phi_{j\vec{k'}}(\vec{r'}) \right] && (63) \\ &= \sum_{\vec{k'}} \sum_{ij} P^{\sigma}_{\vec{k'},ji} \langle p_{\vec{k}} i_{\vec{k'}} | q_{\vec{k}} j_{\vec{k'}} \rangle && (64) \\ &= \sum_{\vec{k'}} \sum_{ij} P^{\sigma}_{\vec{k'},ji} (p_{\vec{k}} q_{\vec{k}} | i_{\vec{k'}} j_{\vec{k'}}). && (65) \end{aligned}$$

Note that all of the $e^{i\vec{k}\cdot\vec{r}}$ factors cancel out in (63). Evaluating the ERI explicitly,[4]

[4] Let $\vec{r} = (r_x, r_y),\ r' = (r'_x, r'_y),\ \vec{G} = (G_x, G_y)$, then

$$|\vec{r} - r'| = \sqrt{(r_x - r'_x)^2 + (r_y - r'_y)^2}$$
$$\vec{G} \cdot (\vec{r} - r') = G_x(r_x - r'_x) + G_y(r_y - r'_y)$$

$$\begin{aligned} \int d^2\vec{r}\ \frac{1}{|\vec{r}-r'|}\ e^{i\vec{G}\cdot(\vec{r}-\vec{r'})} &= \int dr_x dr_y\ \frac{e^{i[G_x(r_x - r'_x) + G_y(r_y - r'_y)]}}{\sqrt{(r_x - r'_x)^2 + (r_y - r'_y)^2}} \quad \text{(substitute } u_i = r_i - r'_i \implies dr_i = du_i) \\ &= \int du_x du_y\ \frac{e^{i[G_x u_x + G_y u_y]}}{\sqrt{u_x^2 + u_y^2}} \\ &= \int d^2\vec{u}\ \frac{e^{i\vec{G}\cdot\vec{u}}}{|\vec{u}|} \quad \text{(use polar coords, } x\text{-axis along } \vec{G}) \\ &= \int_0^{\infty} \int_0^{2\pi} u\ du\ d\theta\ \frac{e^{iGu\cos(\theta)}}{u} \quad \text{(Mathematica)} \\ &= \frac{2\pi}{|\vec{G}|}. \end{aligned}$$

Also see Eq (D2) in Appendix D of [3] and Eq (35) of [4].

$$
\begin{aligned}
(p_{\vec{k}} q_{\vec{k}} | i_{\vec{k}'} j_{\vec{k}'}) &= \int_\Omega d^2\vec{r}\; d^2 r' \;\; \phi^*_{p\vec{k}}(\vec{r})\phi_{q\vec{k}}(\vec{r}) \frac{1}{|\vec{r} - r'|} \phi^*_{i\vec{k}'}(r')\phi_{j\vec{k}'}(r') \\
&= \frac{1}{\Omega} \int d^2\vec{r}\; \phi^*_{p\vec{k}}(\vec{r})\phi_{q\vec{k}}(\vec{r}) \left[\int d^2 r' \;\; \frac{1}{|\vec{r} - r'|} \;\; e^{i(\vec{G}_j - \vec{G}_i)\cdot r'} \right] \\
&= \frac{1}{\Omega} \int_\Omega d^2\vec{r}\; \phi^*_{p\vec{k}}(\vec{r})\phi_{q\vec{k}}(\vec{r}) \;\; e^{i(\vec{G}_j - \vec{G}_i)\cdot\vec{r}} \underbrace{\left[\int_\Omega d^2 r' \;\; \frac{1}{|r' - \vec{r}|} \;\; e^{i(\vec{G}_j - \vec{G}_i)\cdot(r' - \vec{r})} \right]}_{\frac{2\pi}{|\vec{G}_j - \vec{G}_i|}} \\
&= \frac{1}{\Omega^2} \int_\Omega d^2\vec{r}\; e^{i[(\vec{G}_q - \vec{G}_p) + (\vec{G}_j - \vec{G}_i)]\cdot\vec{r}} \cdot \frac{2\pi}{|\vec{G}_j - \vec{G}_i|} \\
&= \frac{1}{\Omega} \cdot \delta(\vec{G}_j + \vec{G}_q - \vec{G}_i - \vec{G}_p) \cdot \frac{2\pi}{|\vec{G}_j - \vec{G}_i|} \\
&= \frac{2\pi}{\Omega |\vec{G}_j - \vec{G}_i|} \;\; \underbrace{\delta[(\vec{G}_j + \vec{G}_q) - (\vec{G}_i + \vec{G}_p)]}_{\text{momentum conservation}}.
\end{aligned} \tag{66}
$$

This gives us

$$
\begin{aligned}
J^\sigma_{\vec{k},pq} &= \frac{2\pi}{\Omega} \sum_{\vec{k}'} \sum_{ij} P^\sigma_{\vec{k}',ji} \frac{1}{|\vec{G}_j - \vec{G}_i|} \;\; \delta[(\vec{G}_j + \vec{G}_q) - (\vec{G}_i + \vec{G}_p)] \\
&= \frac{2\pi}{\Omega} \sum_{\vec{k}'} \sum_{j} P^\sigma_{\vec{k}';j,j+(q-p)} \frac{1}{|\vec{G}_j - (\vec{G}_j + \vec{G}_q - \vec{G}_p)|} \\
&= \frac{2\pi}{\Omega |\vec{Q}|} \sum_{\vec{k}'} \sum_{j} P^\sigma_{\vec{k}';j,j-Q},
\end{aligned} \tag{67}
$$

where we have defined the momentum transfer vector $\vec{Q} = \vec{G}_p - \vec{G}_q$.

3.1.3 The exchange potential, $K^\sigma_{\vec{k}}(\vec{r})$

From Eq 3.320 in [2], the exchange potential is defined with

$$
K^{\sigma\sigma'}_{n\vec{k}}(\vec{r}) \underbrace{\phi_{j\vec{k}'}(\vec{r})}_{\text{AO}} = \left\{ \int d^2\vec{r'} \;\; \psi^{\sigma *}_{n\vec{k}}(\vec{r'}) \frac{1}{|\vec{r} - \vec{r'}|} \phi_{j\vec{k}'}(\vec{r'}) \right\} \underbrace{\psi^{\sigma'}_{n\vec{k}}(\vec{r})}_{\text{MO}} \tag{68}
$$

$$
K^{\sigma\sigma'}(\vec{r}) = \sum_{\vec{k}} \sum_{n,\text{occ}} K^{\sigma\sigma'}_{n\vec{k}}(\vec{r}). \qquad \text{(total exchange potential)} \tag{69}
$$

In the plane wave basis, we have

$$
\begin{aligned}
K^{\sigma\sigma'}_{\vec{k},pq} &= \int_\Omega d^2\vec{r}\; \phi^*_{p\vec{k}}(\vec{r}) K^{\sigma\sigma'}(\vec{r}) \phi_{q\vec{k}}(\vec{r}) \\
&= \int_\Omega d^2\vec{r}\; \phi^*_{p\vec{k}}(\vec{r}) \sum_{\vec{k}'} \sum_{n,\text{occ}} \left\{ \int d^2\vec{r'} \;\; \psi^{\sigma *}_{n\vec{k}'}(\vec{r'}) \frac{1}{|\vec{r} - \vec{r'}|} \phi_{q\vec{k}}(\vec{r'}) \right\} \psi^{\sigma'}_{n\vec{k}'}(\vec{r}).
\end{aligned} \tag{70}
$$

Expanding $\psi^{\sigma}_{n\vec{k}'}(\vec{r}) = \sum_i c^{\sigma}_{n\vec{k}',i}\phi_{i\vec{k}'}(\vec{r})$,

$$\begin{aligned}
K^{\sigma\sigma'}_{\vec{k},pq} &= \sum_{\vec{k}'}\sum_{n,\mathrm{occ}} \int_\Omega d^2\vec{r} \int d^2\vec{r'}\ \phi^*_{p\vec{k}}(\vec{r}) \left\{\sum_i c^{\sigma}_{n\vec{k}',i}\phi_{i\vec{k}'}(\vec{r'})\right\}^* \frac{1}{|\vec{r}-\vec{r'}|}\phi_{q\vec{k}}(\vec{r'}) \left\{\sum_j c^{\sigma'}_{n\vec{k}',j}\phi_{j\vec{k}'}(\vec{r})\right\} \\
&= \sum_{\vec{k}'}\sum_{ij} \left[\sum_{n,\mathrm{occ}} c^{\sigma}_{n\vec{k}',j}\left(c^{\sigma'}_{n\vec{k}',i}\right)^*\right] \left[\int_\Omega d^2\vec{r}\int d^2\vec{r'}\ \phi^*_{p\vec{k}}(\vec{r})\phi^*_{i\vec{k}'}(\vec{r'})\frac{1}{|\vec{r}-\vec{r'}|}\phi_{j\vec{k}'}(\vec{r})\phi_{q\vec{k}}(\vec{r'})\right] \\
&= \sum_{\vec{k}'}\sum_{ij} P^{\sigma\sigma'}_{\vec{k}',ji}\ \langle p_{\vec{k}} i_{\vec{k}'} | j_{\vec{k}'} q_{\vec{k}}\rangle \\
&= \sum_{\vec{k}'}\sum_{ij} P^{\sigma\sigma'}_{\vec{k}',ji}\ \underbrace{(p_{\vec{k}} j_{\vec{k}'} | i_{\vec{k}'} q_{\vec{k}})}_{\circledast}.
\end{aligned} \tag{71}$$

We then need to evaluate $\circledast$:

$$\begin{aligned}
&\int_\Omega d^2\vec{r}\int d^2\vec{r'}\ \phi^*_{p\vec{k}}(\vec{r})\phi^*_{i\vec{k}'}(\vec{r'})\frac{1}{|\vec{r}-\vec{r'}|}\phi_{j\vec{k}'}(\vec{r})\phi_{q\vec{k}}(\vec{r'}) \\
&= \frac{1}{\Omega^2}\int_\Omega d^2\vec{r}\ e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} e^{i(\vec{G}_j-\vec{G}_p)\cdot\vec{r}} \left\{\int d^2\vec{r'}\ e^{i(\vec{k}-\vec{k}')\cdot\vec{r'}}\frac{1}{|\vec{r}-\vec{r'}|}\ e^{i(\vec{G}_q-\vec{G}_i)\cdot\vec{r'}}\right\} \\
&= \frac{1}{\Omega^2}\int_\Omega d^2\vec{r}\ e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} e^{i(\vec{G}_j-\vec{G}_p)\cdot\vec{r}}\ \left\{e^{i[(\vec{G}_q-\vec{G}_i)]+(\vec{k}-\vec{k}')]\cdot\vec{r}}\right\} \left\{\int d^2\vec{r'}\ \frac{1}{|\vec{r'}-\vec{r}|}\ e^{i[(\vec{G}_q-\vec{G}_i)]+(\vec{k}-\vec{k}')]\cdot[\vec{r'}-\vec{r}]}\right\} \\
&= \frac{1}{\Omega^2}\int_\Omega d^2\vec{r}\ \left\{e^{i[(\vec{G}_j-\vec{G}_p)]-(\vec{k}-\vec{k}')]\cdot\vec{r}}\right\}\ \left\{e^{i[(\vec{G}_q-\vec{G}_i)]+(\vec{k}-\vec{k}')]\cdot\vec{r}}\right\} \frac{2\pi}{\left|(\vec{G}_q-\vec{G}_i)+(\vec{k}-\vec{k}')\right|} \\
&= \frac{1}{\Omega^2}\cdot\frac{2\pi}{\left|(\vec{G}_q-\vec{G}_i)+(\vec{k}-\vec{k}')\right|}\int_\Omega d^2\vec{r}\ e^{i[(\vec{G}_j-\vec{G}_p)+(\vec{G}_q-\vec{G}_i)]\cdot\vec{r}} \\
&= \frac{2\pi}{\Omega\left|(\vec{G}_q-\vec{G}_i)+(\vec{k}-\vec{k}')\right|}\ \delta\left[(\vec{G}_j-\vec{G}_p)+(\vec{G}_q-\vec{G}_i)\right].
\end{aligned} \tag{72}$$

This gives us

$$K^{\sigma\sigma'}_{\vec{k},pq} = \frac{2\pi}{\Omega}\sum_{\vec{k}'}\sum_{ij} P^{\sigma\sigma'}_{\vec{k}',ji}\frac{1}{\left|(\vec{G}_q-\vec{G}_i)+(\vec{k}-\vec{k}')\right|}\ \delta\left[(\vec{G}_j-\vec{G}_p)+(\vec{G}_q-\vec{G}_i)\right]. \tag{73}$$

Let us define the momentum transfer vector $\vec{Q} = \vec{G}_q - \vec{G}_i$. Since the momentum index q is fixed, the sum over i involving $1/|\vec{G}_q - \vec{G}_i|$ is just a sum over $\vec{Q}$:

$$\begin{aligned}
K^{\sigma}_{\vec{k},pq} &= \frac{2\pi}{\Omega}\sum_{\vec{k}'}\sum_{Qj} P^{\sigma\sigma'}_{\vec{k}',j,q-Q}\frac{1}{\left|\vec{Q}+(\vec{k}-\vec{k}')\right|}\ \delta\left[(\vec{G}_j-\vec{G}_p)+\vec{Q}\right] \\
&= \frac{2\pi}{\Omega}\sum_{\vec{k}'}\sum_{Q} P^{\sigma\sigma'}_{\vec{k}',p-Q,q-Q}\frac{1}{\left|\vec{Q}+(\vec{k}-\vec{k}')\right|}.
\end{aligned} \tag{74}$$

Compared to $J^{\sigma}_{\vec{k}}$, $K^{\sigma\sigma'}_{\vec{k}}$ is dependent on $\vec{k}$ through $1/|\vec{Q}+(\vec{k}-\vec{k}')|$.

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