

Hartree-Fock for the uniform electron gas

Patryk Kozłowski

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1 Bases

We are working with a basis of plane waves that must be normalized. We do this by enforcing the following condition:

$$\int_{\Omega} d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}} = \int_{\Omega} d\mathbf{r} = L^3 \rightarrow \phi_{\mu}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}_{\mu}\cdot\mathbf{r}} \quad (1)$$

We also know that different plane waves with different wave vectors, but that satisfy the same boundary condition, must be orthogonal, so:

$$\int_{\Omega} d\mathbf{r} \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) = \delta_{\mu\nu} \quad (2)$$

2 Hamiltonian

Now, we want to derive the expressions for the ERI operators in the 3D case. We know that the hearty operator in hearty folk theory in first quantization is defined by:

$$J_n(\mathbf{r}) = \int d\mathbf{r}' \psi_n^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_n(\mathbf{r}') \quad (3)$$

So in total it is given by:

$$J(\mathbf{r}) = \sum_{N_{occ}} J_n(\mathbf{r}) \quad (4)$$

In the plain wave bases, its matrix a limit is given by

$$J_{\mu\nu} = \int_{\Omega} d\mathbf{r} \phi_{\mu}^*(\mathbf{r}) \left(\sum_{N_{occ}} \int d\mathbf{r}' \psi_n^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_n(\mathbf{r}') \right) \phi_{\nu}(\mathbf{r}) \quad (5)$$

Plugging in equation ?? we get:

$$J_{\mu\nu} = \sum_{N_{occ}} \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \psi_n^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_n(\mathbf{r}') \phi_{\nu}(\mathbf{r}) \quad (6)$$

We know that the molecular orbitals $\psi_n^{\sigma}(\mathbf{r})$ are given by a linear combination of the plane waves as $\psi_n(\mathbf{r}) = \sum_i c_{n,i} \phi_i(\mathbf{r})$. Plugging this into the expression for $J_{\mu\nu}$ we get:

$$J_{\mu\nu} = \sum_{N_{occ}} \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \left(\sum_{\lambda} c_{n,\lambda}^* \phi_{\lambda}(\mathbf{r}') \right) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left(\sum_{\sigma} c_{n,\sigma} \phi_{\sigma}(\mathbf{r}') \right) \phi_{\nu}(\mathbf{r}) \quad (7)$$

Bringing the two sums over atomic orbitals and their coefficients out to the front, we get:

$$J_{\mu\nu} = \sum_{\lambda\sigma} \left(\sum_{N_{occ}} (c_{n,\lambda}^* c_{n,\sigma}) \right) \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \phi_{\lambda}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{\nu}(\mathbf{r}) \phi_{\sigma}(\mathbf{r}') \quad (8)$$

In the first stricter formulation, we simplify to

$$J_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma} \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \phi_{\lambda}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{\nu}(\mathbf{r}) \phi_{\sigma}(\mathbf{r}') \quad (9)$$

Defining the ERI as

$$(\mu\nu|\lambda\sigma) = \int_{\Omega} d\mathbf{r} \int d\mathbf{r}' \phi_{\mu}^*(\mathbf{r}) \phi_{\lambda}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{\nu}(\mathbf{r}) \phi_{\sigma}(\mathbf{r}') \quad (10)$$

We know this simplifies to

$$(\mu\nu|\lambda\sigma) = \frac{4\pi}{\Omega} \int d\mathbf{q} \frac{1}{|\mathbf{q}|^2} \delta_{\mathbf{q}, \mathbf{G}_{\mu} - \mathbf{G}_{\nu}} \delta_{\mathbf{q}, \mathbf{G}_{\lambda} - \mathbf{G}_{\sigma}} \quad (11)$$

With the delta functions this integral can be simplified to

$$(\mu\nu|\lambda\sigma) = \frac{4\pi}{\Omega} \frac{1}{|\mathbf{G}_{\mu} - \mathbf{G}_{\nu}|^2} \delta_{\mathbf{G}_{\mu} - \mathbf{G}_{\nu}, \mathbf{G}_{\lambda} - \mathbf{G}_{\sigma}} \quad (12)$$

Now, for the exchange term, now the spin is relevant and we fast forward to

$$K_{\mu\nu}^{\sigma} = \sum_{\lambda\sigma} P_{\lambda\sigma}^{\sigma} (\mu\sigma|\lambda\nu) \quad (13)$$

The integral is now

$$(\mu\sigma|\lambda\nu) = \frac{4\pi}{\Omega} \int d\mathbf{q} \frac{1}{|\mathbf{q}|^2} \delta_{\mathbf{q}, \mathbf{G}_\mu - \mathbf{G}_\sigma} \delta_{\mathbf{q}, \mathbf{G}_\lambda - \mathbf{G}_\nu} = \frac{4\pi}{\Omega} \frac{1}{|\mathbf{G}_\mu - \mathbf{G}_\sigma|^2} \delta_{\mathbf{G}_\mu - \mathbf{G}_\sigma, \mathbf{G}_\lambda - \mathbf{G}_\nu} \quad (14)$$

and we have the following expression for the exchange term:

$$K_{\mu\nu}^\sigma = \sum_\lambda P_{\lambda\sigma}^\sigma (\mu\sigma|\lambda\nu) = \frac{4\pi}{\Omega} \sum_\lambda P_{\lambda\sigma}^\sigma \frac{1}{|\mathbf{G}_\mu - \mathbf{G}_\sigma|^2} \delta_{\mathbf{G}_\mu - \mathbf{G}_\sigma, \mathbf{G}_\lambda - \mathbf{G}_\nu} \quad (15)$$

2.0.1 Alternative derivation

We can derive the two-electron term in another way. We know this is given by

$$\hat{V}_{ee} = \frac{1}{2\Omega} \sum_{G_1 G_2 G_3 G_4} \frac{4\pi}{|G_2 - G_3|^2} a_{G_1}^\dagger a_{G_2}^\dagger a_{G_3} a_{G_4} \quad (16)$$

We know that the total momentum transfer must be conserved, so $G_1 + G_2 = G_3 + G_4$, and $G_4 = G_1 + G_2 - G_3$. Defining $Q = G_2 - G_3$, we know that $G_4 = G_1 + Q$, whereas then $G_3 = G_2 - Q$. Redefining $G_1 \equiv G$ and $G_2 \equiv G'$, we can write the two-electron term as:

$$\hat{V}_{ee} = \frac{1}{2\Omega} \sum_{GG'Q} \frac{4\pi}{|Q|^2} a_G^\dagger a_{G'}^\dagger a_{G'-Q} a_{G+Q} \quad (17)$$

Applying Wick's theorem gives:

$$\hat{V}_{ee} = \frac{1}{2\Omega} \sum_{GG'Q} \frac{4\pi}{|Q|^2} (P_{G, G+Q} P_{G', G'-Q} - P_{G, G'-Q} P_{G', G+Q}), \quad (18)$$

where we use the usual definition that $\langle a_{G_1}^\dagger a_{G_2} \rangle = P_{G_1, G_2}$, which is the density matrix. We are just interested in the second term for exchange, which is

$$\Sigma_x = -\frac{1}{2\Omega} \sum_{GG'} \Lambda_{GG'} \quad (19)$$

where we defined

$$\Lambda_{GG'} = \sum_Q \frac{4\pi}{|Q|^2} P_{G, G'-Q} P_{G', G+Q} \quad (20)$$

Here we might have the similar thing with the Fourier transform of $1/|\mathbf{r}|$ being $\frac{2\pi}{\mathbf{q}}$ and the two-electron integral simplifying to:

$$g_{\mu\lambda\nu\sigma} = \frac{2\pi}{A} \frac{1}{|\mathbf{k}_\mu - \mathbf{k}_\lambda|} \delta_{\mathbf{k}_\mu - \mathbf{k}_\lambda, \mathbf{k}_\sigma - \mathbf{k}_\nu} \quad (21)$$

3 Kinetic energy

We started by specifying a kinetic energy cutoff. In atomic units, the kinetic energy of a plane wave is given by:

$$, E_{\text{kinetic}} = \frac{\mathbf{k}^2}{2} \quad (22)$$

Now if we try to evaluate \mathbf{k}^2 for a plane wave with wave vector $\mathbf{k} = (k_x, k_y, k_z)$, we get:

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) \quad (23)$$

where L is the length of the box and n_x, n_y, n_z are integers. In terms of the Wigner-Seitz radius r_s , the volume of the cell is given by the volume of the sphere of a single electron multiplied by the number of electrons

$$V = \left(\frac{4\pi N}{3}\right) r_s^3 \quad (24)$$

We can approximate it as a box with the same volume and $V = L^3$. So, we get an expression for L as:

$$L = \left(\frac{4\pi N}{3}\right)^{1/3} r_s \quad (25)$$

Let $C = \frac{1}{2} \left(\frac{2\pi}{L}\right)^2$. Plugging this into the expression for E_{kinetic} we get:

$$E_{\text{kinetic}} = C (n_x^2 + n_y^2 + n_z^2) = C (n_x^2) + C (n_y^2 + n_z^2) \quad (26)$$

Therefore, we know that the kinetic energy cut off should scale with as $N^{-2/3}$ and r_s^{-2} .

3.1 2D case

As before the kinetic energy of a plain wave is given by the same thing:

$$E_{\text{kinetic}} = \frac{\mathbf{k}^2}{2} \quad (27)$$

Now if we try to evaluate \mathbf{k}^2 for a plane wave with wave vector $\mathbf{k} = (k_x, k_y)$, we get:

$$k^2 = k_x^2 + k_y^2 = \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2) \quad (28)$$

where L is the length of the box and n_x, n_y are integers. In terms of the Wigner-Seitz radius r_s , the area of the cell is given by the area of the circle of a single electron multiplied by the number of electrons

$$A = \pi N r_s^2 \quad (29)$$

We can approximate it as a box with the same area and $A = L^2$. So, we get an expression for L as:

$$L = \sqrt{\pi N} r_s \quad (30)$$

Plugging this into the expression for E_{kinetic} we get:

$$E_{\text{kinetic}} = \frac{1}{2} \left(\frac{2\pi}{\sqrt{\pi N} r_s} \right)^2 (n_x^2 + n_y^2) = 2\pi N^{-1} r_s^{-2} (n_x^2 + n_y^2) \quad (31)$$

4 SCF procedure

The Fermi energy is defined as the energy at which the probability of finding an electron is 1/2. In the uniform electron gas, the Fermi energy is the energy of the HOMO and is given in natural units as:

$$E_F = \frac{\left(\frac{9\pi^4}{16}\right)^{2/3}}{r_s^2} \quad (32)$$

Once we specify the kinetic energy cutoff, we are left with a number of valid plane wave basis states N_{PW} . We construct the kinetic and Coulomb matrices using this basis. For the initial guess of the one-electron density matrix in

the restricted formalism, we just have its diagonal filled with 2s up to $N_{\text{elec}}/2$ and 0s for the rest.

$$P_{\mu\nu}^{(0)} = \begin{cases} 2 & \text{if } \mu = \nu \leq N_{\text{elec}}/2 \\ 0 & \text{otherwise} \end{cases} \quad (33)$$

Next, we construct a Fock matrix with:

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left(g_{\mu\lambda\nu\sigma} - \frac{1}{2} g_{\mu\nu\sigma\lambda} \right) \quad (34)$$

and then diagonalize it to get the new orbital coefficients $C_{\mu i}$ and the single particle energies ε_i :

$$\varepsilon_i = h_{ii} + \sum_a^{N_{\text{elec}}/2} (2J_{ia} - K_{ia}) \quad (35)$$

We also construct a new density matrix using the new orbital coefficients:

$$P_{\mu\nu} = 2 \sum_{i=1}^{N_{\text{elec}}/2} C_{\mu i} C_{\nu i} \quad (36)$$

The convergence criteria are for the change in energy and the norm of the density matrix between iterations to be minimal. The formular for the restricted Hartree-Fock energy is not just the sum of the single particle energies, because this double counts the electron-electron repulsion. The correct formula is:

$$E_{HF} = \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}/2} (\varepsilon_i + h_{ii}) \quad (37)$$

Then there is the Madeleung constant two take into account that just provides a correction to the energy:

$$E_M \approx -2.837297 \times \left(\frac{3}{4\pi} \right)^{1/3} N^{2/3} r_{\pi}^{-1} \quad (38)$$

By plugging in the single protocol energy, we see that this simplifies to:

$$E_{HF} = \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}/2} \left(h_{ii} + \sum_a^{N_{\text{elec}}/2} (2J_{ia} - K_{ia}) + h_{ii} \right) = \sum_{i=1}^{N_{\text{elec}}/2} h_{ii} + \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}/2} \sum_a^{N_{\text{elec}}/2} (2J_{ia} - K_{ia}) \quad (39)$$

which is NOT the same as:

$$\sum_{i=1}^{N_{\text{elec}}/2} \varepsilon_i = \sum_{i=1}^{N_{\text{elec}}/2} h_{ii} + \sum_{i=1}^{N_{\text{elec}}/2} \sum_a^{N_{\text{elec}}/2} (2J_{ia} - K_{ia}) \quad (40)$$

we can also equivalently write the energy as:

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_v P_{vu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \quad (41)$$

In order to determine the spin polarization, we know that $N_{\alpha} + N_{\beta} = N_{\text{elec}}$ and $\rho = \frac{N_{\alpha} - N_{\beta}}{N_{\text{elec}}}$, where N_{α} and N_{β} are the number of alpha and beta electrons respectively with spin polarization ρ . Solving these coupled equations gives

$$N_{\alpha} = \frac{N_{\text{elec}}}{2} (1 + \rho) \quad N_{\beta} = \frac{N_{\text{elec}}}{2} (1 - \rho) \quad (42)$$

5 SCF convergence with DIIS

The idea is that we want to keep a certain "cache" of the results from previous iterations, in order to accelerate convergence of the iterative procedure. Starting with an initial guess for the density matrix P_0 , we calculate the Fock matrix F_0 and corresponding energy E_0 of the first iteration. By diagonalizing this initial Fock matrix we can construct a density matrix for the next iteration as P_1 and send this to the guess for the next iteration. We can then calculate the Fock matrix F_1 and energy E_1 for the next iteration. This is the procedure for the classical SCF, but now we want to use DIIS. Now we want to save a certain number of Fock matrices from previous iterations in order to construct a new density matrix. So we want the Fock matrix at the k -th iteration to be a linear combination of some number of previous Fock matrices

$$F_k = \sum_{i=(k-1)-j}^{k-1} c_i F_i, \quad (43)$$

where j indicates the number that we want to keep. The goal is to minimize the residual factor R_k which is defined as:

$$R_k = F_k P_k S - S P_k F_k$$