Average Exchange Energy

The following is a reprise of the derivation of the Kohn-Sham exchange potential given in Ref. [1]. Let us consider an N electron atom and suppose that a given state can be described by a single determinental wave function $\Psi_{abc\cdots}$. The energy of the atom in this state can be written

$$E = \sum_a \langle a|h_0|a\rangle + \frac{1}{2}\sum_{ab}\iint \frac{d^3r_1 d^3r_2}{R}\phi_a^\dagger(r_1)\phi_a(r_1)\phi_b^\dagger(r_2)\phi_b(r_2)$$
$$-\frac{1}{2}\sum_{ab}\iint \frac{d^3r_1 d^3r_2}{R}\phi_a^\dagger(r_1)\phi_b(r_1)\phi_b^\dagger(r_2)\phi_a(r_2)\,. \qquad (1)$$

The term on the second line of Eq. (1) is the exchange energy $E_{\rm exch}$. The exchange energy is evaluated assuming that the single-particle orbitals are non-relativistic plane waves:

$$\phi_a(r) = \frac{1}{\sqrt{V}}e^{ip_a\cdot r}\chi_{\sigma_a}\,.$$

We find

$$E_{\rm exch} = -\frac{1}{2V^2}\sum_{\sigma_a\sigma_b}\left(\chi^\dagger_{\sigma_a}\chi_{\sigma_b}\right)\left(\chi^\dagger_{\sigma_b}\chi_{\sigma_a}\right)\sum_{p_a p_b}\iint \frac{d^3r_1 d^3r_2}{R}e^{iq\cdot R}\,, \qquad (2)$$

with $q = p_b - p_a$ and $R = r_1 - r_2$. We make use of the fact that

$$\frac{1}{V}\sum_{p_a} \rightarrow \frac{1}{(2\pi)^3}\int d^3p_a\,,$$

and

$$\sum_{\sigma_a\sigma_b}\left(\chi^\dagger_{\sigma_a}\chi_{\sigma_b}\right)\left(\chi^\dagger_{\sigma_b}\chi_{\sigma_a}\right) = \sum_{\sigma_a}\left(\chi^\dagger_{\sigma_a}\chi_{\sigma_a}\right) = 2\,,$$

to rewrite the expression for the exchange energy as

$$E_{\rm exch} = -\frac{1}{(2\pi)^6}\iint d^3r_1 d^3r_2 \iint d^3p_a d^3p_b \frac{1}{R}e^{iq\cdot R}\,. \qquad (3)$$

Change variables to $R = r_1 - r_2$, and $r = r_2$; then $d^3r_1 d^3r_2 = d^3R d^3r$ and the exchange energy becomes

$$E_{\rm exch} = -\frac{1}{(2\pi)^6}\int d^3r \iint d^3p_a d^3p_b \int \frac{d^3R}{R}e^{iq\cdot R}\,. \qquad (4)$$

One can evaluate the innermost integral (with damping at large R) as

$$\int \frac{d^3R}{R}e^{iq\cdot R} = \frac{4\pi}{q^2}. \qquad (5)$$

It follows that

$$E_{\text{exch}} = -\frac{2}{(2\pi)^4} \int d^3r \int d^3p_a \int_0^{p_f} p_b^2 dp_b \int_{-1}^{1} \frac{d\mu}{p_a^2 + p_b^2 - 2p_a p_b \mu} . \tag{6}$$

The integral over μ can be carried out to give

$$\int_{-1}^{1} \frac{d\mu}{p_a^2 + p_b^2 - 2p_a p_b \mu} = \frac{1}{p_a p_b} \ln\left(\frac{p_a + p_b}{|p_a - p_b|}\right) . \tag{7}$$

The integral over p_b is next carried out to give

$$\int_0^{p_f} dp_b \frac{p_b}{p_a} \ln\left(\frac{p_a + p_b}{|p_a - p_b|}\right) = \frac{1}{2p_a}\left[\left(p_f^2 - p_a^2\right) \ln\left(\frac{p_f + p_a}{p_f - p_a}\right) + 2p_f p_a\right] . \tag{8}$$

The integral over d^3p_a is next carried out to give

$$2\pi \int_0^{p_f} dp_a\, p_a \left[\left(p_f^2 - p_a^2\right) \ln\left(\frac{p_f + p_a}{p_f - p_a}\right) + 2p_f p_a\right] = 2\pi p_f^4 \tag{9}$$

This gives us finally,

$$E_{\text{exch}} = -\frac{2}{(2\pi)^3} \int d^3r\, p_f^4 = -\frac{3}{4\pi}(3\pi^2)^{1/3} \int d^3r \rho^{4/3}(r) , \tag{10}$$

where we have used the relation

$$p_f = (3\pi^2 \rho(r))^{1/3}$$

to express the Fermi-momentum in terms of the particle density.

Variational Equations

We may express the energy of a system of particles in terms of the electronic wave functions as

$$E = \int d^3r \left\{ \sum_a \phi_a^\dagger h_0 \phi_a + \frac{1}{2} \int \frac{d^3r' \rho(r)\rho(r')}{R} - \frac{3}{4\pi}(3\pi^2)^{1/3} \rho^{4/3}(r) \right\} , \tag{11}$$

where

$$\rho(r) = \sum_a |\phi_a(r)|^2 . \tag{12}$$

In our discussion, we require

$$N_a = \int d^3r |\phi_a(r)|^2 = 1 .$$

The variation $\delta\phi_a^\dagger$ in the single-particle orbital ϕ_a leads to the variation

$$\delta\left[E-\epsilon_a N_a\right] = \int d^3r\,\delta\phi_a^\dagger\left\{h_0\phi_a+\int\frac{d^3r'\,\rho(r')}{R}\phi_a-\left[\frac{3}{\pi}\rho(r)\right]^{1/3}\phi_a-\epsilon_a\phi_a\right\}, \quad (13)$$

in $E-\epsilon_a N_a$, where ϵ_a is a Lagrange multiplier introduced to insure that the normalization constraint is satisfied. The condition $\delta\left[E-\epsilon_a N_a\right]=0$ leads to the Kohn-Sham equations

$$\left(h_0+\int\frac{d^3r'\,\rho(r')}{R}+v_{\rm exch}(r)\right)\phi_a=\epsilon_a\phi_a\,, \quad (14)$$

where

$$v_{\rm exch}(r)=-\left[\frac{3}{\pi}\rho(r)\right]^{1/3}. \quad (15)$$

As shown in [1], the Kohn-Sham exchange potential is related to the average exchange potential introduced earlier by Slater [2] by

$$v_{\rm exch}(r)=\frac{2}{3}v_{\rm Slater}\,.$$

Practical Matters

In numerical codes, one deals with the radial parts $P_a(r)$ of the orbitals $\phi_a(r)$,

$$\phi_a(r)\equiv\phi_{n_a l_a m_a \sigma_a}(r)=\frac{1}{r}P_{n_a l_a}(r)Y_{l_a m_a}(\hat{r})\chi_{\sigma_a}\,, \quad (16)$$

which are normalized by

$$\int_0^\infty dr\,\left[P_{n_a l_a}(r)\right]^2=1\,. \quad (17)$$

The corresponding radial density for the atom is

$$n(r)=\sum_a g_a P_a^2(r)\,, \quad (18)$$

where g_a is the occupation number of the subshell $a\equiv(n_a l_a)$. Averaging over angles, one obtains

$$\int_0^\infty dr\,n(r)=N\,, \quad (19)$$

where N is the total number of electrons in the atom. We write the density in terms of the radial density as

$$\rho(r)=\frac{1}{4\pi r^2}n(r)\,, \quad (20)$$

and consequently

$$v_{\rm exch}(r)=-\left[\frac{3}{4\pi^2}\frac{n(r)}{r^2}\right]^{1/3}. \quad (21)$$

References

[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] J. C. Slater, Phys. Rev. **81**, 385 (1951).