Letter

Exchange and correlation in the Thomas–Fermi approximation

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We present the exchange and correlation potential calculated analytically as a function of the Hartree potential. We arrived at this expression by using the Thomas–Fermi approximation. This is an alternative way of calculating the exchange and correlation potential which can be very efficient.

There are many papers about the study of the effects of many bodies in the calculation of atoms, molecules, clusters and solid states. In most cases, our starting point is the one-electron approach and we simply assume that the effect of many bodies generates a variation of the one-electron potential, that we commonly call exchange and correlation potential. Due to the difficulties found in real systems these potentials must be obtained numerically by means of long and complex self-consistent calculations [2,4–7].

The use of the Thomas–Fermi (TF) approximation to calculate the energy spectrum in atoms is standard now [5]. Recently, the use of that theory in solid state calculations has given very good results [1,3]. In this way, it was possible to obtain a self-consistent potential in analytical form, thus providing a very useful tool for the theoretical study of these systems.

The present work intends to provide a procedure for the calculation of the exchange and correlation potential as a function of the Hartree potential. It will be seen that this is the simplest way to obtain this potential.

We shall assume to be in the low temperature limit. In an ideal, uniform electron gas, the number of electrons per unit volume is

$$n = \frac{2}{(2\pi)^3}\frac{4\pi}{3}\frac{p_F^3}{\hbar^3} = \frac{1}{3\pi^2}\frac{p_F^3}{\hbar^3}, \tag{1}$$

where p_F is the radius of the Fermi sphere in the momentum space. If we consider the gas as locally homogeneous, i.e., that the ideal gas approximation is valid at each

point, we have

$$n(\mathbf{r}) = \frac{1}{3\pi^2} \frac{p_F^3(\mathbf{r})}{\hbar^3}. \tag{2}$$

The probability $I_r(\vec{p})\,d\vec{p}$ that the momentum of the electron has a value between p and $p + dp$ is

$$I_r(\vec{p})\,d\vec{p} = \frac{4\pi p^2\,dp}{(4/3)\pi p_F^3}\theta(p_F - p). \tag{3}$$

The kinetic energy per unit volume, t say, is

$$t = \frac{1}{2\pi^2 m\hbar^3}\int_0^{p_F} p^4\,dp = \frac{\hbar^2[3\pi^2 n(\mathbf{r})]^{5/3}}{10\pi^2 m}. \tag{4}$$

The kinetic energy functional is

$$T = \int t\,d\mathbf{r} = \frac{3}{10m}\int n(\mathbf{r})\big[3\pi^2\hbar^3 n(\mathbf{r})\big]^{2/3}\,d\mathbf{r}, \tag{5}$$

and the energy functional which corresponds to the electron–electron interaction is

$$V_{ee} = \frac{e^2}{2\varepsilon_r}\iint \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'. \tag{6}$$

Here it is assumed that the electrons are in a homogeneous medium of dielectric constant ε_r (the so-called *hydrogenic model*).

Therefore, the TF energy-density functional is given by

$$E_{TF} = \frac{3}{10m}\int n(\mathbf{r})\big[3\pi^2\hbar^3 n(\mathbf{r})\big]^{2/3}\,d\mathbf{r} + \frac{e^2}{2\varepsilon_r}\iint \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'. \tag{7}$$

It is known that the variational principle leads to $\delta(E_{TF} - \mu N) = 0$, where $N = \int n(\mathbf{r})\,d\mathbf{r}$ and μ is the Lagrange multiplier. Calculating the variational by the standard procedure we find

$$\mu = \frac{1}{2m}\big[3\pi^2\hbar^3 n(\mathbf{r})\big]^{2/3} + \frac{e^2}{2\varepsilon_r}\int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}', \tag{8}$$

but, taking into account that

$$V_H(\mathbf{r}) = \frac{e^2}{2\varepsilon_r}\int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}', \tag{9}$$

it is possible to write

$$\mu = \frac{1}{2m}\big[3\pi^2\hbar^3 n(\mathbf{r})\big]^{2/3} + V_H(\mathbf{r}) \tag{10}$$

and, finally,

$$n(\mathbf{r}) = \frac{1}{3\pi^2\hbar^3}(2m)^{3/2}\big(\mu - V_H(\mathbf{r})\big)^{3/2}. \tag{11}$$

The exchange potential in the local density approximation is

$$V_x(\mathbf{r}) = -\left(\frac{2}{\pi\alpha r_s(\mathbf{r})}\right)R_y^*, \tag{12}$$

where

$$r_s(\mathbf{r}) = \left(4\pi a^* n(\mathbf{r})/3\right)^{-1/3}, \tag{13}$$

the effective Bohr radius $a^* = 4\pi\varepsilon_r\hbar^2/me^2$, $\alpha = [4/(9\pi)]^{1/3}$ and the effective Rydberg constant $R_y^* = e^2/(8\pi\varepsilon_r a^*)$.

If equation (10) is used in (12), we have

$$r_s(\mathbf{r}) = \left(\frac{4a^*}{9\pi}\right)^{-1/3}\frac{\hbar}{(2m)^{1/2}}\left(\mu - V_{\mathrm{H}}(\mathbf{r})\right)^{-1/2}, \tag{14}$$

then

$$V_x(\mathbf{r}) = -\frac{2a^{*1/3}}{\pi}\frac{(2m)^{1/2}}{\hbar}\left(\mu - V_{\mathrm{H}}(\mathbf{r})\right)^{1/2}R_y^*, \tag{15}$$

and if we have an analytical expression for the Hartree potential, then we should obtain an analytical expression for the exchange and correlation potential, too. If one wishes to make a numerical self-consistent calculation, and one has an initial potential, one has an initial exchange and correlation potential too.

The total potential, $V(\mathbf{r}) = V_{\mathrm{H}}(\mathbf{r}) + V_x(\mathbf{r})$, is

$$V(\mathbf{r}) = V_{\mathrm{H}}(\mathbf{r}) - \frac{2a^{*1/3}}{\pi}\frac{(2m)^{1/2}}{\hbar}\left(\mu - V_{\mathrm{H}}(\mathbf{r})\right)^{1/2}R_y^*. \tag{16}$$

The exchange and correlation potential is given as a function of r_s, thus if we have an analytical expression of the Hartree potential it follows that we can also have an analytical expression for the exchange and correlation potential.

In conclusion, we have presented one method to calculate the exchange and correlation potential as a function of the Hartree potential. This is an alternative approach to the Kohn–Sham scheme and always serves as a first approximation to the real exchange and correlation potential.

Acknowledgements

References

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