Química Cuántica de Sólidos
Tarea 04: Teoría del funcional de la densidad

Dr. Omar De la Peña Seaman

04 octubre 2024

Nombre del Estudiante: ____

Problema 1 *Thomas-Fermi method*

In the Thomas-Fermi model, the kinetic energy functional is approximated to the free-electron gas system, as

$$T[n(\mathbf{r})] = c_1 \int d\mathbf{r} n(\mathbf{r})^{5/3} \ \ \forall \ \ c_1 = \frac{3}{10}(3\pi^2)^{2/3}.$$

Obtain the value of c_1 under that model.

. . . .

Problema 2 *Electron density*

If the electronic density can be expressed as,

$$n(\mathbf{r}) = \langle\psi|\hat{n}(\mathbf{r})|\psi\rangle \ \ \forall \ \ \hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r}),$$

demonstrate that $n(\mathbf{r})$ can be also:

$$n(\mathbf{r}) = N \int d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N |\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 \ \ \forall \ \ \mathbf{x}_\alpha \equiv \mathbf{r}_\alpha, s.$$

Hint: $\int \delta(\mathbf{r}_1 - \mathbf{r}) f(\mathbf{r}_1) d\mathbf{r}_1 = f(\mathbf{r})$.

. . . .

Problema 3 *Kinetic energy functional for spin-polarized systems*

Considering the Kohn-Sham kinetic-energy funcional of a polarized-system, as:

$$T[n_\uparrow, n_\downarrow] = \sum_i \sum_\sigma \langle\psi_i^\sigma| -\frac{1}{2}\nabla^2 |\psi_i^\sigma\rangle,$$

where $\sigma =\uparrow, \downarrow$ and i is the particle-label, whith the spin densities given by:

$$n_\sigma(\mathbf{r}) = \sum_i |\psi_i^\sigma(\mathbf{r})|^2,$$

then, demonstrate the following:

1) The kinetic-energy funcional can be expressed as,

$$T[n_\uparrow, n_\downarrow] = \frac{1}{2}T[2n_\uparrow] + \frac{1}{2}T[2n_\downarrow].$$

2) In view that the fractional spin-polarization ζ is constant over all space,

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n} \quad \forall \quad n = n_\uparrow + n_\downarrow,$$

then,

$$T[n_\uparrow, n_\downarrow] = \frac{1}{2}\left[(1+\zeta)^{5/3} + (1-\zeta)^{5/3}\right] T_0[n],$$
$$\forall \quad T_0[n] = \frac{3}{10}(3\pi^2)^{2/3}\int d\mathbf{r} n^{5/3}.$$

Hint: G.L. Oliver, J.P. Perdew, *Phys. Rev. A* **20**, 397 (1979).

. . . .

Problema 4 *Exchange-correlation functional: LDA*

For the LDA formulation, demonstrate that the exchange in a polarized system has the following form,

$$\epsilon_x(n,\zeta) = \epsilon_x(n,0) + [\epsilon_x(n,1) - \epsilon_x(n,0)]\, f_x(\zeta),$$
$$\forall \quad f_x(\zeta) = \frac{1}{2}\frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{1/3}-1},$$

where n and ζ are the total density and fractional polarization, respectively.
Hint: U. von Barth and L. Hedin, *J. Phys. C: Solid State Phys.* **5**, 1629 (1972).

. . . .

Problema 5 *Hellmann-Feynman theorem*

Consider the following Schrödinger equation,

$$\hat{H}\psi = E\psi,$$

assume that all involved quantities depend on some parameter λ, and that ψ is normalized:

$$\langle\psi|\psi\rangle = 1.$$

Demonstrate the following:

$$\frac{dE}{d\lambda} = \frac{d}{d\lambda}\langle\psi|\hat{H}|\psi\rangle = \langle\psi|\frac{d\hat{H}}{d\lambda}|\psi\rangle\,,$$

which is the Hellmann-Feynman theorem.
Hint: Consider that the Hamilton operator is hermitian and that the energy is real.

. . . .