Quantum Chemistry: week 4 (2020)

Question 1

We rehearse the free electron gas. We start with free particles: they don't have interaction with anything. They only have kinetic energy. The solutions are plane waves:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \quad , \quad \mathbf{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Here Ω is the volume we use for normalization. We work with fixed Ω, but beware: for the real free electron gas we have to take the limit $\Omega \to \infty$.

(a) Show that the $\phi_{\mathbf{k}}(\mathbf{r})$ are eigen functions of the Hamiltonian, and obtain the eigenvalues $\epsilon_{\mathbf{k}}$. Beware: $\mathbf{k}$ is a vector.

Answ: The Hamiltonian is just the kinetic energy operator. Just apply it to the plane wave:

$$-\frac{\hbar^2}{2m_e}\nabla^2\left(e^{i(k_x x+k_y y+k_z z)}\right) = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\left(e^{i(k_x x+k_y y+k_z z)}\right) =$$
$$-\frac{\hbar^2}{2m_e}(-k_x^2-k_y^2-k_z^2)e^{i(k_x x+k_y y+k_z z)} = \frac{\hbar^2|\mathbf{k}|^2}{2m_e}e^{i(k_x x+k_y y+k_z z)} = e_{\mathbf{k}}e^{i(k_x x+k_y y+k_z z)}$$

Here we didn't bother to normalize. Denoting $k = |\mathbf{k}|$ for the length of the vector, we have:

$$e_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_e}$$

(b) Next we apply periodic boundary conditions (PBC). We take a cube, with edge length L, so $\Omega = L^3$. The PBC now say that:

$$\begin{aligned} \phi_{\mathbf{k}}(x+L,y,z) &= \phi_{\mathbf{k}}(x,y,z) \quad \text{and} \\ \phi_{\mathbf{k}}(x,y+L,z) &= \phi_{\mathbf{k}}(x,y,z) \quad \text{and} \\ \phi_{\mathbf{k}}(x,y,z+L) &= \phi_{\mathbf{k}}(x,y,z) \end{aligned}$$

What values of k_x, k_y and k_z are allowed?

Answ: First note that the eigenfunction factorizes, i.e. x, y and z dependencies are independent:

$$e^{i(k_x x+k_y y+k_z z)} = e^{ik_x x}e^{ik_y y}e^{ik_z z}$$

The PBC for x require:

$$e^{ik_x(x+L)} = e^{ik_x x} \Rightarrow k_x L = 2\pi n_x \quad , \quad n_x = 0,\ 1,\ 2,\ 3,\ 4,\ 5,\ \ldots \tag{1}$$

This has to be because the complex exponent attains the same value for every multiple of 2π added to its argument.

(c) Explicitly show that our solutions, normalized in the volume Ω and with PBC according to (b), are orthonormal:

$$\int_\Omega \phi_{\mathbf{k}}(\mathbf{r})^*\phi_{\mathbf{k}'}(\mathbf{r})\,d\mathbf{r} = \delta_{\mathbf{k},\mathbf{k}'}$$

Answ: Just write out explicitly:

$$\int_\Omega \phi^*_{\mathbf{k}}(\mathbf{r})\phi_{\mathbf{k}'}\,d\mathbf{r} = \frac{1}{\Omega}\int_0^L\int_0^L\int_0^L e^{i(k'_x-k_x)x}e^{i(k'_y-k_y)y}e^{i(k'_z-k_z)z}\,dx\,dy\,dz$$

If $\mathbf{k} = \mathbf{k}'$, the product of exponents becomes 1, so the integral yields Ω and the matrix element just equals 1. For $\mathbf{k} \neq \mathbf{k}'$ it is sufficient that either $k_x \neq k'_x$ or $k_y \neq k'_y$ or $k_z \neq k'_z$. We just consider the first, the others run similar:

$$\int_0^L e^{i(k'_x - k_x)x}\, dx = \left[\frac{e^{i(k'_x - k_x)x}}{i(k'_x - k_x)}\right]_0^L = \frac{e^{i((2\pi/L)n'_x - (2\pi/L)n_x)L} - 1}{i(k'_x - k_x)} = \frac{e^{2\pi i(n'_x - n_x)} - 1}{i(k'_x - k_x)} = 0$$

where the last step follows because $n'_x - n_x$ is integer (and because the denominator is non-vanishing, as $n'_x \neq n_x$).

(d) The Fermi energy ϵ_F defines the boundary between occupied and empty states. Why is it associated with a sphere in the 3 dimensional "$\mathbf{k}$-space"?

Answ: $\epsilon_\mathbf{k}$ only depends on the length k of the vector $\mathbf{k}$, it increases with the distance k to the origin. So all occupied states have $|\mathbf{k}| = k < k_\mathrm{F}$ with

$$\epsilon_\mathrm{F} = \frac{\hbar^2 k_\mathrm{F}^2}{2m_e} \tag{2}$$

(e) We are now going to count states. How large is the $\mathbf{k}$-space volume associated with a single state? Knowing you're dealing with a sphere of occupied states, use this and the formula for the volume of a sphere to obtain the total number of states N with $\epsilon_\mathbf{k} < \epsilon_\mathrm{F}$. First express your result in terms of the Fermi wave vector $\mathbf{k}_\mathrm{F}$.

Answ: First we count. One state corresponds to $\Delta n_x = \Delta n_y = \Delta n_z = 1$. Using (1) we see that this corresponds to a volume per state of $(2\pi)^3/L^3 = (2\pi)^3/\Omega$.

We have to count all states within a sphere with a radius k_F that is given by (2). The volume of this sphere is $(4/3)\pi k_\mathrm{F}^3$. We obtain the number of states dividing this volume by the volume per state. We need an additional factor 2 to account for spin:

$$N = 2\frac{(4/3)\pi k_\mathrm{F}^3}{(2\pi)^3/\Omega} = \frac{\Omega k_\mathrm{F}^3}{3\pi^2}$$

We can use (2) to write this as a function of the Fermi energy:

$$N = \frac{\Omega}{3\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \epsilon_\mathrm{F}^{3/2}$$

(f) Calculate the total energy of the system, given the Fermi velocity $\mathbf{k}_\mathrm{F}$, and show that

$$E = \frac{3}{5} N \epsilon_\mathrm{F} \tag{3}$$

Answ: We have to integrate over the volume of the sphere, counting at each point the energy of the state. As usual we convert to an integral (which becomes exact for large Ω):

$$E = 2\sum_{k<k_\mathrm{F}} \epsilon_\mathbf{k} = 2\frac{\Omega}{(2\pi)^3}\int_{<k_\mathrm{F}} \epsilon_\mathbf{k}\, d\mathbf{k}$$

Here we have divided by the volume per state $(2\pi)^3/\Omega$ when converting to the integral. $d\mathbf{k}$ denotes a volume element. We exploit spherical symmetry: first integrate over the surface of a sphere and after that radially:

$$E = 2\frac{\Omega}{(2\pi)^3}\int_0^{k_\mathrm{F}} \epsilon_\mathbf{k}\, 4\pi k^2\, dk = 2\frac{\Omega}{(2\pi)^3}\int_0^{k_\mathrm{F}} \frac{\hbar^2 k^2}{2m_e}\, 4\pi k^2\, dk = \frac{\Omega\hbar^2 k_\mathrm{F}^5}{10\pi^2 m_e} = \frac{3}{5}\frac{\Omega k_\mathrm{F}^3}{3\pi^2}\frac{\hbar^2 k_\mathrm{F}^2}{2m_e} = \frac{3}{5} N\epsilon_\mathrm{F}$$

Here the known expressions for N and ϵ_F were used.

(g) We now look at the same problem, but in Hartree-Fock:

$$\left[\frac{p^2}{2m_e} + V_{\text{ion}} + e^2\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' - e^2\int \frac{\rho_i^X(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Here "V_{ion}" is the potential of the uniform positive background density. Why does it exactly cancel the "Hartree" term?

Answ: Obvious, follows...

(h) We focus on the non-local exchange charge density:

$$\rho_i^X(\mathbf{r},\mathbf{r}') = \sum_j \frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})}{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})}$$

Apply this expression for our plane wave solutions.

Answ: Same as notes.

(i) A delta function can be written as the integral of complex exponents:

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\,dk$$

where k and x just denote general variables. Use this to show that:

$$\frac{1}{(2\pi)^3}\int d\mathbf{r}' e^{-i(\mathbf{k}-\mathbf{k}'-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{q}-(\mathbf{k}-\mathbf{k}'))$$

So here we generalized to 3 dimensions and we somehow got rid of the $\mathbf{r}$ in de argument of the exponents (how did we do that?)

Answ: To get a feeling for the expression, for any pair $f(x), \tilde{f}(k)$, related via a Fourier transform, we can write:

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\tilde{f}(k)\,e^{ikx}\,dk \Leftrightarrow f(k) = \int_{-\infty}^{\infty} f(x)\,e^{-ikx}\,dx$$

(of course, we have freedom how to accommodate the $1/2\pi$ and where to put the minus). Now we choose $f(x) = \delta(x)$:

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\,dk \Leftrightarrow 1 = \int_{-\infty}^{\infty}\delta(x)\,e^{-ikx}\,dx$$

Here the R.H.S. is obvious, so if we read from right to left, we obtain the given expression for the delta function on the L.H.S.

To proof what we are asked to do: (1) do it per carthesian component, (2) swap the roles of x and k and (3) substitute $k = q_x - k_x + k'_x$. E.g., for the x-component:

$$2: \ \frac{1}{2\pi}\int e^{ikx}dx = \delta(k) \overset{(3)}{\rightarrow} \frac{1}{2\pi}\int e^{i(q_x-k_x+k'_x)x}dx = \delta(q_x - k_x + k'_x)$$

The carthesian components factorize, which brings us at the final result (note that $1/(2\pi)^3$ was missing on the problem sheet).

Question 2

Make a 2-particle Slater determinant and calculate the density $n(\mathbf{r})$ according to:

$$n(\mathbf{r}) = N\int \Psi^*(\mathbf{r},\mathbf{r}_2,\ \ldots,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,\ \ldots,\mathbf{r}_N)\,d\mathbf{r}_2\ldots d\mathbf{r}_N$$

Answ: Let's relabel for convenience ($\mathbf{r} \to \mathbf{r}_1$, $\mathbf{r}' \to \mathbf{r}_2$). The $\psi_i(\mathbf{r})$ are spin-orbitals.

$$\Psi(\mathbf{r},\mathbf{r}') = \Psi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\right]$$

$$\Psi^*(\mathbf{r},\mathbf{r}') = \frac{1}{\sqrt{2}}\left[\psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2) - \psi_2^*(\mathbf{r}_1)\psi_1^*(\mathbf{r}_2)\right]$$

So:

$$\begin{aligned}\Psi^*\Psi = \frac{1}{2}[&\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2) + \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\psi_2^*(\mathbf{r}_1)\psi_1^*(\mathbf{r}_2) \\ &-\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_2^*(\mathbf{r}_1)\psi_1^*(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)]\end{aligned}$$

This we have to integrate over $\mathbf{r}_2$ and multiply with $N = 2$. The contributions from the first line survive, because of normalization of the ψ_i. The contributions from the second line vanish, because of orthogonality of the ψ_i. This either happens in the integratation over $\mathbf{r}_2$ in case the spatial orbitals are orthogonal, or just because to the matrix element of spin part vanishes. So we have ($\mathbf{r}_1 \to \mathbf{r}$):

$$n(\mathbf{r}) = |\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2$$

If this represents two electrons in a singlet in the same orbital $\phi(\mathbf{r})$, this becomes:

$$n(\mathbf{r}) = 2|\phi(\mathbf{r})|^2$$

(Note: this is actually a simpler version of question 3a of week 3.)

Question 3

Which of the following is a functional?
(a) $\mathcal{F}[f(x)] = \sin(f(x))$,

(b) $\mathcal{F}[f(x)] = \int_0^{10} f(x)\,dx$,

(c) $\mathcal{F}[f(x)] = \int_0^{10} |f(x)|\,dx$,

(d) $\mathcal{F}[f(x)] = df(x)/dx|_{x=3}$
For those $\mathcal{F}$ that are a functional, what can you say about that functions f that minimize the functional? And what is the minimum?

(e) Now devise a functional on $[0,\pi]$ that attains of minimum value (of 10) for the function $f(x) = \cos(8x)$.

Note: We did not yet discuss functionals this week. Remember that a function is a recipe to turn the value of an input variable into a number. Given an input variable x, the function f yields a single-valued output $f(x)$. In brief: $x \to f(x)$. A functional is something similar, but now the input is a function itself. The output is still a number. In brief: $f \to \mathcal{F}[f]$, where f is a function and $\mathcal{F}[f]$ yields a number. A very simple example: $\mathcal{F}[f(x)] = 0$. That just yields 0, whatever function you put in.
Answ: (a) $\sin(f(x))$ is not a functional. It does not yield a number as output if you put in a function. Instead, it yields a new function.

(b) $\int_0^{10} f(x)\,dx$ is a functional. You put in a function, then integration over a finite interval yields one number (for $f(x)$ sufficiently well-behaved). Note there is no minimum: Suppose you have $f(x) = C$, with C a constant. Then $F[f(x)] = 10C$. You can choose an arbitrarily low (negative) value of C.

(c) $\int_0^{10} |f(x)|\,dx$ is also a functional. Also here you get a number out for a function as input. The number cannot be negative, because you integrate the absolute value. So the minimum is 0, which is attained for the function $f(x) = 0$.

(d) $df(x)/dx|_{x=3}$ is also a functional, because the derivative at $x = 3$ is a single number as output. There is no minimum. You can choose a function $f(x) = Cx$ with arbitrarily steep negative slope C

at $x = 0$.

(e) For example:

$$\mathcal{F}[f(x)] = 10 + \int_0^\pi \left(f(x) - \cos(8x)\right)^2 \, dx$$

If you put in $f(x) = \cos(8x)$ *the integral yields 0, so* $\mathcal{F}[f(x)] = 10$. *For any other function there are* x *for which is* $f(x) - \cos(8x)$ *is not 0. For those* $\left(f(x) - \cos(8x)\right)^2$ *will be larger than 0. Hence* $\mathcal{F}[f(x)] > 10$.

Of course we had to assume that the functions are are "well-behaved", i.e. continuous.