PHY 555: Solid-state Physics I

Homework #5-6
Due: 12/08/2025

Homework is due by the end of the due date specified above. ***Late homework will be subject to 3 points off per day past the deadline, please contact me if you anticipate an issue making the deadline.*** *It should be turned in via blackboard. For the conceptual and analytical parts, turn in a scan or picture of your answers (please ensure that they are legible) or an electronic copy if done with, e.g., LaTeX. For the computational part, turn in your source code and a short description of your results (including plots). The description can be separate (e.g., in LaTeX or word), or combined (e.g., in a jupyter notebook). Let me know if you are not sure about the format.*

Conceptual

1. ***5 points*** Explain what the one-electron approximation is and how Hartree-Fock and density-functional theory go beyond it.
2. ***5 points*** Compare and contrast Hartree-Fock and density-functional theory in terms of the following aspects:
   (**a**) General philosophy for addressing the many-electron problem.
   (**b**) The resulting single-electron problem to solve.
   (**c**) The physical interpretation of the auxiliary single-particle orbitals and eigenvalues.

Analytical

3. ***20 points*** In class we discussed the Fermi energy E_F and density of states (DOS) for the free-electron gas in three dimensions.
   (**a**) Determine the average energy per electron (in class denoted as E_0/N) for the 1D and 2D free electron gasses.
   (**b**) Determine the DOS for the free-electron gas in one and two dimensions. Schematically plot the energy dependence of the DOS.
   (**c**) To leading order in T, what is the temperature dependence of the Fermi energy in the 1D free-electron gas? What happens if we try to use the Sommerfeld expansion to linear order for the T-dependence of the Fermi energy in 2D?
   (**d**) Find the T dependence of E_F for the 2D case (without using the Sommerfeld expansion) by calculating

$$N = 2\left(\frac{L}{2\pi}\right)^2 \int f(E) d^2k, \tag{1}$$

   relating N to $E_\mathrm{F}(T=0)$ and solving for $E_\mathrm{F}(T)$. Show that the result is discontinuous at $T=0$, and hence the Sommerfeld expansion does not apply.
4. ***25 points*** We have discussed plane waves and atomic orbitals for performing calculations of the electronic structure of solids and materials. In addition, *gaussians* are another common basis set, and useful for other calculations in solids. The benefit of gaussians as a basis set is that they are localized functions, so do not require pseudopotentials like plane waves, and integrals are easier to calculate

than atomic orbitals. For example, one of the useful property about gaussians is the *gaussian product theorem* (GPT) that states that the product of two gaussians is also a gaussian, centered at the "center of gravity" of the two original gaussians. I.e., for $\chi_a(\mathbf{r}) = e^{-\alpha(\mathbf{r}-\mathbf{A})^2}$ and $\chi_b(\mathbf{r}) = e^{-\beta(\mathbf{r}-\mathbf{B})^2}$,

$$\chi_a(\mathbf{r})\chi_b(\mathbf{r}) = e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{P})^2} \tag{2}$$

where $\mathbf{P} = (\alpha\mathbf{A} + \beta\mathbf{B})/(\alpha+\beta)$.

(a) Consider a basis set of gaussians of the form $\phi_i(\mathbf{r}) = A_i e^{\alpha_i|\mathbf{r}-\mathbf{R}_i|^2}$. Using the GPT [Eq. (2)], show that we can calculate the overlap between gaussians, i.e., $S_{ij} = \int \phi_i(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r}$ with the simple relation

$$S_{ij} = A_i A_j e^{-\frac{\alpha_i\alpha_j}{\alpha_i+\alpha_j}(\mathbf{R}_i-\mathbf{R}_j)^2} \left(\frac{\pi}{\alpha_i+\alpha_j}\right)^{3/2} \tag{3}$$

Note that we neglect the complex conjugation since all gaussians considered here will be real.

(b) In general Coulomb matrix elements, for V_{ext} and the two electron integrals, are tricky to calculate. This is because we need to be careful integrating over divergences of the form $1/|\mathbf{r}-\mathbf{r}'|$ when $\mathbf{r} = \mathbf{r}'$. With gaussians, there is an elegant way to evaluate these matrix elements, utilizing the integral transformation

$$\frac{1}{|\mathbf{r}-\mathbf{R}_C|} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-|\mathbf{r}-\mathbf{R}_C|^2 t^2} dt \tag{4}$$

Consider a gaussian charge density $\rho_i(\mathbf{r}) = (\alpha_i/\pi)^{3/2}\exp(-\alpha_i|\mathbf{r}-\mathbf{R}_i|^2)$, which could correspond to a basis function, or product of basis functions (both are gaussians!). Show using the result of **(a)** that $\rho_i(\mathbf{r})$ is normalized to unity. Then, using Eq. (4) and Eq. (2), show that the electrostatic potential at point $\mathbf{R}_C$, i.e.,

$$V_i(\mathbf{R}_C) = \int \frac{\rho_i(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_C|} d\mathbf{r} \tag{5}$$

can be written as

$$V_i(\mathbf{R}_C) = \frac{1}{|\mathbf{R}_i-\mathbf{R}_C|} \operatorname{erf}\left(\sqrt{\alpha_i|\mathbf{R}_i-\mathbf{R}_C|^2}\right), \tag{6}$$

where erf is the error function and we use atomic units throughout so $m_e = e = \hbar = 1$. ***Hint:*** One way to proceed is to first perform the integral over $\mathbf{r}$, and then make the change of variables from t to $u = t/\sqrt{\alpha_i + t^2}$; then relate the resulting expression to the integral definition of the error function: $\operatorname{erf}(z) = \sqrt{\frac{4}{\pi}} \int_0^z e^{-\tau^2} d\tau$.

(c) Using the result of **(b)** and Eq. (2), show that an arbitrary Coulomb matrix element between gaussians

$$U_{ijkl} = \int\int \frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_k(\mathbf{r}_2)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \tag{7}$$

can be written as

$$U_{ijkl} = \frac{S_{ij}S_{kl}}{|\mathbf{R}_{ij}-\mathbf{R}_{kl}|} \operatorname{erf}\left(\sqrt{\omega_{ijkl}|\mathbf{R}_{ij}-\mathbf{R}_{kl}|^2}\right) \tag{8}$$

where $\mathbf{R}_{ij} = (\alpha_i\mathbf{R}_i + \alpha_j\mathbf{R}_j)/((\alpha_i+\alpha_j)$ (similarly for $\mathbf{R}_{kl}$) and $\omega_{ijkl} = \frac{(\alpha_i+\alpha_j)(\alpha_k+\alpha_l)}{\alpha_i+\alpha_j+\alpha_k+\alpha_l}$.

Computational

5. ***20 points*** In this problem, we consider a simple diatomic molecule made up of a hydrogen atom and a helium atom (H-He) with two electrons. We set the location of H at $\mathbf{R}_{\mathrm{H}} = (0, 0, 0)$ and He is $\mathbf{R}_{\mathrm{He}} = (1.5117, 0, 0)$ Bohr. We use a basis set made up of two Gaussians:

$$\phi_1(\mathbf{r}) = 0.3696e^{-0.4166|\mathbf{r}-\mathbf{R}_{\mathrm{H}}|^2} \tag{9}$$

$$\phi_2(\mathbf{r}) = 0.5881e^{-0.7739|\mathbf{r}-\mathbf{R}_{\mathrm{He}}|^2} \tag{10}$$

We will neglect spin and use atomic units throughout so $m_e = e = \hbar = 1$.

(**a**) Calculate the kinetic energy matrix elements with the basis functions:

$$T_{ij} = \int \phi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \phi_j(\mathbf{r}) d\mathbf{r}. \tag{11}$$

(**b**) Use your results from problem **4** to calculate the matrix elements of the external potential

$$V_{ij} = -\int \phi_i(\mathbf{r}) \frac{Z_{\mathrm{H}}}{|\mathbf{r}-\mathbf{R}_{\mathrm{H}}|} \phi_j(\mathbf{r}) d\mathbf{r} - \int \phi_i(\mathbf{r}) \frac{Z_{\mathrm{He}}}{|\mathbf{r}-\mathbf{R}_{\mathrm{He}}|} \phi_j(\mathbf{r}) d\mathbf{r}. \tag{12}$$

(**c**) Use your results from problem **4** to calculate the Coulomb and exchange matrix elements

$$U_{ijkl} = \int\int \frac{\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_k(\mathbf{r}_2)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \tag{13}$$

(**d**) Calculate the nuclear-nuclear repulsion energy $V_{\mathrm{N}} = Z_{\mathrm{He}}Z_{\mathrm{H}}/|\mathbf{R}_{\mathrm{H}} - \mathbf{R}_{\mathrm{He}}|$.

6. ***20 points*** Now we have all of the information to solve for the energy of the molecule using Hartree-Fock (HF). directly solving the HF equation is challenging, especially because of the exchange term, which makes it an integro-differential equation. For "closed shell" systems where we can neglect the spin part (as we do here), we can actually express the equation in a form much easier to solve:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon}. \tag{14}$$

In this equation, **S** is the overlap matrix between basis functions discussed in problem **4**(**a**); **C** is the matrix of expansion coefficients for the basis elements, i.e., the wavefunctions solving the HF equations will be given by is given by $\psi_j = \sum_i C_{ij}\phi_i$; and **F** is the Fock matrix with elements

$$F_{ij} = T_{ij} + V_{ij} + \sum_{kl} P_{kl}(U_{ijkl} - \frac{1}{2}U_{ilkj}) \equiv T_{ij} + V_{ij} + G_{ij}, \tag{15}$$

where P_{kl} are the elements of the 2×2 "charge density matrix." They are related to the expansion coefficient via

$$P_{kl} = 2\sum_{i}^{N/2} C_{ki}C_{li}^{*}, \tag{16}$$

where N is the number of electrons in the system (in our case there will be two). It is called the charge-density matrix because the total charge density of the system can be written as $\rho(\mathbf{r}) = \sum_{ij} P_{ij}\phi_i(\mathbf{r})\phi_i^{*}(\mathbf{r})$. Perform the following steps to solve for the energy of the H-He molecule using Hartree-Fock:

(**a**) Choose an initial guess for **P** (for example, all elements zero).

(**b**) Calculate **F** using Eq. (15).

(**c**) Solve the generalized eigenvalue problem in Eq. (14). If you are using python, you can use `scipy.linalg.eigh`, e.g., with the line:

```
epsilon, C = scipy.linalg.eigh(F, S, eigvals_only=False)
```

(**d**) Determine an updated **P** using **C** and Eq. (16).

(**e**) Calculate the energy via

$$E = \sum_{ij} P_{ij} \left(F_{ij} - \frac{1}{2} G_{ij} \right) + V_N. \tag{17}$$

(**f**) Repeat steps (**b**)-(**e**) to get an updated guess of the energy. Continue cycling until the energy changes by less than 10^{-5} Ha.