

PHY 555: Solid-state Physics I

Homework #7

Due: 12/09/2022

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. **10 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.
3. **5 points** Explain the adiabatic Born-Oppenheimer approximation used in calculating nuclear dynamics.

Analytical

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 $\chi_b(\mathbf{r}) = e^{-\beta(\mathbf{r}-\mathbf{B})^2}$,

$$\chi_a(\mathbf{r})\chi_b(\mathbf{r}) = e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{P})^2} \quad (1)$$

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. (1)], 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

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

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

$$\frac{1}{|\mathbf{r} - \mathbf{R}_C|} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-|\mathbf{r} - \mathbf{R}_C|^2 t^2} dt \quad (3)$$

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. (3) and Eq. (1), show that the electrostatic potential at point \mathbf{R}_C , i.e.,

$$V_i(\mathbf{R}_C) = \int \frac{\rho_i(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_C|} d\mathbf{r} \quad (4)$$

can be written as

$$V_i(\mathbf{R}_C) = \frac{1}{|\mathbf{R}_i - \mathbf{R}_C|} \text{erf} \left(\sqrt{\alpha_i |\mathbf{R}_i - \mathbf{R}_C|^2} \right), \quad (5)$$

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: $\text{erf}(z) = \sqrt{\frac{4}{\pi}} \int_0^z e^{-\tau^2} d\tau$.

- (c) Using the result of (b) and Eq. (1), show that an arbitrary Coulomb matrix element between gaussians

$$U_{ijkl} = \int \int \frac{\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_k(\mathbf{r}_2) \phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (6)$$

can be written as

$$U_{ijkl} = \frac{S_{ij} S_{kl}}{|\mathbf{R}_{ij} - \mathbf{R}_{kl}|} \text{erf} \left(\sqrt{\omega_{ijkl} |\mathbf{R}_{ij} - \mathbf{R}_{kl}|^2} \right) \quad (7)$$

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

5. **25 points** An important contribution to the energy of ionic materials is the sum of electrostatic interactions between oppositely charged ions. In class we discussed how to describe this in 1D via the Madelung constant, which gave the potential energy of a given reference ion due to the Coulomb interaction with all other positive and negative ions in the crystal. Here we will determine the Madelung constant in higher dimensions via the Ewald method.

- (a) We start by smearing the point charges representing the ion at the origin into a gaussian normalized to $+e$, $\rho(r) = (+e) \left(\frac{\eta}{\pi}\right)^{3/2} e^{-\eta r^2}$ where $r = |\mathbf{r}|$. What is the electrostatic potential $\varphi(\mathbf{r})$ resulting from this charge density?
- (b) Show that $\varphi(0)$ does not diverge, but when $\eta \rightarrow \infty$, the potential becomes the Coulomb potential.
- (c) Consider a crystal with lattice points \mathbf{t}_n , and ions of charge $-e$ at sites \mathbf{t}_n , and charge $+e$ at sites $\mathbf{t}_n + \mathbf{d}$. If we take the ions to be point charges, what is the potential energy $V(\mathbf{r})$ felt by the ion at the origin from all of the other ions?
- (d) Now we use a trick, where we write the Coulomb interaction as $-\frac{e^2}{r} = -\frac{e^2}{r} \left[\text{erf}(\sqrt{\eta r^2}) + \text{erfc}(\sqrt{\eta r^2}) \right]$ where erfc is the complimentary error function defined such that $\text{erf} + \text{erfc} = 1$. Use this to

(trivially) write $V(\mathbf{r})$ as two terms, i.e., $V(\mathbf{r}) = V_1(\mathbf{r}) + V_2(\mathbf{r})$, where $V_1(\mathbf{r})$ involves the erfc terms, and $V_2(\mathbf{r})$ involves the erf terms.

- (e) Argue that $V_1(0)$, which we need for the Madelung constant, is short-ranged in real space. How should we choose η to converge with fewer lattice vectors in the sum?
- (f) Write the second term in the form $V_2(\mathbf{r}) = U(\mathbf{r}) - \frac{e^2}{r} \text{erf}(\sqrt{\eta}r)$, and note that $U(\mathbf{r})$ is a periodic function. Because of this, we can write $U(\mathbf{r})$ as a Fourier series $U(\mathbf{r}) = \sum_{\mathbf{G}_m \neq 0} e^{i\mathbf{G}_m \cdot \mathbf{r}} \tilde{U}(\mathbf{G}_m)$ where $\tilde{U}(\mathbf{G}_m) = \frac{1}{N\Omega} \int e^{-i\mathbf{G}_m \cdot \mathbf{r}} U(\mathbf{r}) d\mathbf{r}$ and $N\Omega$ is the volume of the crystal (note, we neglect the $\mathbf{G}_m = 0$ term, since it should be zero in a charge neutral crystal). Calculate the Fourier coefficients $\tilde{U}(\mathbf{G}_m)$ and use them to show that

$$V_2(0) = \frac{4\pi e^2}{\Omega} \sum_{\mathbf{G}_m \neq 0} \left(1 - e^{i\mathbf{G}_m \cdot \mathbf{d}}\right) \frac{e^{-G_m^2/4\eta}}{G_m^2} - 2e^2 \sqrt{\frac{\eta}{\pi}} \quad (8)$$

where N is number of unit cells in the crystal. Note that this term is short-ranged in *reciprocal space*. How should we choose η to make $V_2(0)$ converge faster, i.e., with fewer reciprocal lattice vectors in the sum?

Hint: Note that the Fourier transform of the error function is given by

$$\int_{-\infty}^{\infty} \frac{e^2}{r} \text{erf}\left(\sqrt{\eta}r\right) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} = \frac{4\pi e^2}{k^2} e^{-k^2/4\eta} \quad (9)$$

6. **20 points** In class we discussed the linear chain with nearest-neighbor interactions, for which the energy within the harmonic approximation is $E = \frac{1}{2} C \sum_n (u_n - u_{n+1})^2$. Now consider the linear chain *without* the assumption of only nearest-neighbor interactions, i.e., with energy

$$E = \sum_n \sum_{m>0} \frac{1}{2} C_m [u_n - u_{n+m}]^2. \quad (10)$$

- (a) Show that the dispersion relation in this case is

$$\omega(q) = 2 \sqrt{\sum_{m>0} C_m \frac{\sin^2[mqa/2]}{M}} \quad (11)$$

- (b) Show that the long-wavelength limit is proportional to $|q|$.

- (c) Show that your result from (b) for the small q behavior of $\omega(q)$ will diverge if $C_m = 1/m^p$ where $1 < p < 3$. In this case, we can use another approach to determine the long-wavelength limit: replace the sum over m in Eq. (11) with an integral since at small q , the wavelength is very large compared to the interatomic spacing. Use this approach to show that for $p = 3/2$, $\omega(q) \propto q^{1/4}$.

7. **20 points** So far, we have only considered classical lattice dynamics. We now treat the quantum counterpart, using the example of the monatomic linear chain. Then the nuclear Hamiltonian is

$$H = \sum_n \frac{1}{2M} p_n^2 + \frac{1}{2} C \sum_n (2u_n^2 - u_n u_{n+1} - u_n u_{n-1}) \quad (12)$$

where now u_n and p_n are the coordinate and conjugate momentum of the nucleus at the n th site, which obey the commutation relations $[u_n, p_{n'}] = i\hbar \delta_{n,n'}$ and $[u_n, u_{n'}] = [p_n, p_{n'}] = 0$.

(a) Consider the phonon creation and annihilation operators defined as

$$a_q = \frac{1}{\sqrt{N}} \sum_{t_n} e^{-iqt_n} \left[u_n \sqrt{\frac{M\omega(q)}{2\hbar}} + ip_n \sqrt{\frac{1}{2\hbar M\omega(q)}} \right] \quad (13)$$

$$a_q^\dagger = \frac{1}{\sqrt{N}} \sum_{t_n} e^{iqt_n} \left[u_n \sqrt{\frac{M\omega(q)}{2\hbar}} - ip_n \sqrt{\frac{1}{2\hbar M\omega(q)}} \right], \quad (14)$$

where we will later choose $\omega(q)$ to diagonalize H . Show that the transformation from u_n, p_n to a_q, a_q^\dagger is canonical, i.e., that the commutation rules are preserved. Specifically, $[a_q, a_{q'}^\dagger] = \delta_{q,q'}$ and $[a_q, a_{q'}] = [a_q^\dagger, a_{q'}^\dagger] = 0$.

(b) Show that

$$u_n = \frac{1}{\sqrt{N}} \sum_q \sqrt{\frac{\hbar}{2M\omega(q)}} e^{iqt_n} [a_q + a_{-q}^\dagger] \quad (15)$$

$$p_n = \frac{-i}{\sqrt{N}} \sum_q \sqrt{\frac{\hbar M\omega(q)}{2}} e^{iqt_n} [a_q - a_{-q}^\dagger] \quad (16)$$

(c) Now plug these expressions into Eq. (12). Also, we can use a trick where we set

$$\omega(q) = \frac{C}{M\omega(q)} (2 - e^{iqa} - e^{-iqa}), \quad (17)$$

in the potential energy term (where a is the atomic spacing). This is equivalent to saying $\omega^2(q) = \frac{C}{M} (2 - e^{iqa} - e^{-iqa})$ which is what we found for the classical case. Show that this results in the Hamiltonian of the linear chain expressed as

$$H = \sum_q \hbar\omega(q) \left(a_q^\dagger a_q + \frac{1}{2} \right) \quad (18)$$

Hint: Recall the following expressions that may be useful:

$$\frac{1}{N} \sum_{t_n} e^{-i(q-q')t_n} = \delta_{q,q'} \quad (19)$$

$$\frac{1}{N} \sum_q e^{-iq(t_n - t_{n'})} = \delta_{n,n'} \quad (20)$$

Computational

8. **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 $\mathbf{R}_H = (0,0,0)$ and He is $\mathbf{R}_{He} = (1.5117, 0, 0)$ Bohr. We use a basis set made up of two Gaussians:

$$\phi_1(\mathbf{r}) = 0.3696e^{-0.4166|\mathbf{r}-\mathbf{R}_H|^2} \quad (21)$$

$$\phi_2(\mathbf{r}) = 0.5881e^{-0.7739|\mathbf{r}-\mathbf{R}_{He}|^2} \quad (22)$$

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:

$$T_{ij} = \int \phi_i(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \phi_j(\mathbf{r}) d\mathbf{r}. \quad (23)$$

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

$$V_{ij} = - \int \phi_i(\mathbf{r}) \frac{Z_H}{|\mathbf{r} - \mathbf{R}_H|} \phi_j(\mathbf{r}) d\mathbf{r} - \int \phi_i(\mathbf{r}) \frac{Z_{He}}{|\mathbf{r} - \mathbf{R}_{He}|} \phi_j(\mathbf{r}) d\mathbf{r}. \quad (24)$$

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

$$U_{ijkl} = \int \int \frac{\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_k(\mathbf{r}_2) \phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (25)$$

(d) Calculate the nuclear-nuclear repulsion energy $V_N = Z_{He}Z_H/|\mathbf{R}_H - \mathbf{R}_{He}|$.

9. **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:

$$\mathbf{FC} = \mathbf{SC}\epsilon. \quad (26)$$

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

$$F_{ij} = T_{ij} + V_{ij} + \sum_{kl} P_{kl} (U_{ijkl} - \frac{1}{2} U_{ilkj}) \equiv T_{ij} + V_{ij} + G_{ij}, \quad (27)$$

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

$$P_{kl} = 2 \sum_i^{N/2} C_{ki} C_{li}^*, \quad (28)$$

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 $\rho(\mathbf{r}) = \sum_{ij} P_{ij} \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r})$. Perform the following steps to solve for the energy of the H-He molecule using Hartree-Fock:

(a) Choose an initial guess for \mathbf{P} (for example, all elements zero).

(b) Calculate \mathbf{F} using Eq. (27).

(c) Solve the generalized eigenvalue problem in Eq. (26). 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 \mathbf{P} using \mathbf{C} and Eq. (28).

(e) Calculate the energy via

$$E = \sum_{ij} P_{ij} \left(F_{ij} - \frac{1}{2} G_{ij} \right) + V_N. \quad (29)$$

(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.