

Problem 1. Correlation and Exchange Potential

As discussed in class, the general Hamiltonian for electrons in a system of static nuclei is given by

$$H = \sum_i \left[\frac{\mathbf{p}_i^2}{2m} + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (1)$$

In this problem, we will explore this Hamiltonian for the relatively simple problem of H_2 in order to identify the classical and nonclassical effects of spin. In this problem, the nuclei are separated along a particular axis $\mathbf{d} = d\hat{\mathbf{z}}$, and we will assume that we have solved the single-particle problem, finding that the most important low-energy orbitals are symmetric and anti-symmetric combinations of s-orbitals

$$\chi_{\pm}(\mathbf{r}) = \mathcal{N}_{\pm}(\psi_L(\mathbf{r}) \pm \psi_R(\mathbf{r})), \quad \psi_L(\mathbf{r}) = \psi_s(\mathbf{r} - \mathbf{d}/2), \quad \psi_R(\mathbf{r}) = \psi_s(\mathbf{r} + \mathbf{d}/2). \quad (2)$$

By assumption, these solve $(\frac{\mathbf{p}^2}{2m} + V_{\text{ext}}(\mathbf{r}))\chi_{\pm}(\mathbf{r}) = E_{\pm}\chi_{\pm}(\mathbf{r})$, and we define $2t = E_- - E_+ > 0$. With spin, there are four states $\chi_{\pm}(\mathbf{r})|\uparrow\rangle$ and $\chi_{\pm}(\mathbf{r})|\downarrow\rangle$.

- Assuming $\psi_s(\mathbf{r}) \propto e^{-r^2/(4a_0^2)}$, find the normalizations \mathcal{N}_{\pm} . **Note: s-orbitals do not have this form, we are only assuming this for convenience.**
- If $\chi_{\pm}(\mathbf{r})|\uparrow\rangle$ and $\chi_{\pm}(\mathbf{r})|\downarrow\rangle$ are the only relevant single-particle wavefunctions, write down all two-particle, fermionic wavefunctions (be mindful of the spin degree of freedom). What is the Hilbert-space dimension of this two-particle space?
- In the above two-particle basis, what are the matrix elements of the single-particle part of the Hamiltonian? $H = \frac{1}{2m}\mathbf{p}_1^2 + V_{\text{ext}}(\mathbf{r}_1) + \frac{1}{2m}\mathbf{p}_2^2 + V_{\text{ext}}(\mathbf{r}_2)$
- Write down the integral expressions for the matrix elements of the interaction term $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ in the same basis (in terms of $\chi_{\pm}(\mathbf{r})$). Which ones are zero? Which terms do you expect to be large? Note that on the diagonal, some terms are proportional to densities and others have wavefunctions *exchanged*. (**Hint:** It may be useful to transform your basis from Part (b) into one that is purely symmetric or antisymmetric in the spin-basis.)
- Without evaluating the integrals, what can we say about the *spin configuration* of the ground state?

Problem 2. Spin-orbit coupling

If we treat our electrons relativistically, electrons obey the 4×4 Dirac Hamiltonian

$$H_D = \begin{pmatrix} mc^2 + V(\mathbf{r}) & (c\mathbf{p} - e\mathbf{A}) \cdot \boldsymbol{\sigma} \\ (c\mathbf{p} - e\mathbf{A}) \cdot \boldsymbol{\sigma} & -mc^2 + V(\mathbf{r}) \end{pmatrix}, \quad V(\mathbf{r}) = -e\phi(\mathbf{r}). \quad (3)$$

In this problem, we will derive the low-energy Hamiltonian with relativistic corrections

- (a) Given $\Psi = (\psi_e \ \psi_p)^T$ for two-component spinors ψ_e and ψ_p and $H_D\Psi = E\Psi$, find an equation for the electrons ψ_e and expand it assuming c is large, keeping terms up to $1/c^2$.
- (b) Assume that the potential term is only dependent on the radius. Show that the spin-orbit coupling term derived in Part (a) takes the form

$$h_{\text{SOC}} = \xi(r)\mathbf{L} \cdot \mathbf{S}, \quad \mathbf{S} = \frac{1}{2}\boldsymbol{\sigma}, \quad (4)$$

and evaluate what $\xi(r)$ is in terms of $\phi(r)$.

- (c) Assume that $\phi(r) = Ze/r$, and evaluate $\langle h_{\text{SOC}} \rangle$ for wave functions with principle quantum number n , angular momentum ℓ , total angular momentum j , and spin s . (Hint: $\langle 1/r^3 \rangle = 2Z^3/(a_0^3 n^3 \ell(\ell+1)(2\ell+1))$ for the Bohr radius a_0). What does this begin to tell us about the elements Z for which this term is relevant? In a material like Bi_2Se_3 “spin-orbit coupling is important,” but which atom’s spin-orbit coupling?

Problem 3. Delta function lattice and edge states

Crystals have bulk states and if there is a boundary, they can have *edge* states. Edge states are important for topology, but their sole existence is not a proof of topology, as we illustrate in this problem. We will remain in one-dimension for this problem.

- (a) For a particle in the periodic potential of the form, $U(x) = \alpha \sum_{n=-\infty}^{\infty} \delta(x - na)$ (this potential can be viewed as a model of an ideal one-dimensional “crystal”), find a system of independent solutions of the Schroedinger equation for an arbitrary value of E and determine the energy spectrum.
- (b) Find the energy spectrum and degeneracy of levels of a particle in the potential of the form

$$U(x) = \begin{cases} \alpha \sum_{n=1}^{\infty} \delta(x - na), & x > 0, \\ U_0 > 0, & x \leq 0. \end{cases} \quad (5)$$

Compare your results from Part (a). Pay special attention to the appearance of states, localized near the boundary of the crystal. These states, you will find, are called *surface* or *Tamm* states, and they play an important role in semiconductor physics.