

Homework 13

Due in class Thursday, Dec. 6

1. If we take the $e-e$ interaction to be a perturbation in the helium atom, then the zero-th order eigenstates are just hydrogenic solutions with $Z = 2$ when spin-orbit and higher-order interactions are neglected.

- (a) Write down the ground singlet and triplet states (properly symmetrized and angular momentum eigenstates!). Argue that orbital and spin angular momenta are separately conserved.
- (b) Calculate to first order the shifts to the states in (a) due to the electron-electron interaction. Do the directions of the shifts make sense? (HINT: Consider the two-electron density.)
- (c) Repeat (a) and (b) for the H^- ion. Is H^- stable in this approximation, or is it more favorable to break up into $\text{H}+e$? (The one with lower energy is more favorable.)

2. Use the variational principle to find an approximation to the ground state energy of He (*i.e.* the $1s^2\ ^1S$ state). Use a hydrogenic trial function for each electron, but take the charge in the function to be an effective charge, Z_{eff} , which will be the variational parameter. In this way, the variational procedure takes into account the screening of the nucleus by the other

- (a) Write down the ground singlet trial function (make sure it is properly symmetrized and is an angular momentum eigenstate!).
- (b) Find the optimal Z_{eff} — and thus the approximate ground state energy — for He. Compare with the exact result (see Table 1).
- (c) Repeat (b) for the H^- ion. Is H^- stable in this approximation, or is it more favorable to break up into $\text{H}+e$? Is H^- stable in reality?
- (d) Repeat again for Li^+ . How does your energy compare to the exact energy of Li^+ ? Is your variational result getting better or worse as the charge of the nucleus is increased? Discuss your answer physically in terms of what physics is important and what physics your wave function includes.
- (e) Are your variational energies better than the perturbative ones from Prob. 1? Should they be? Discuss the comparison physically — *i.e.*, what physics does the better approximation include that the other does not.

3. Apply the variational principle to find the low-lying spectrum of

$$V(x) = \begin{cases} \infty & |x| > a \\ 10\frac{\hbar^2}{ma^2}\frac{x}{a} & |x| \leq a \end{cases}.$$

In particular, use the expansion

$$\psi(x) = \sum_{n=1}^N a_n \phi_n(x)$$

where $\{\phi_n(x)\}$ are the infinite square well eigenstates, and answer the following questions:

- (a) First, sketch a picture of the potential with what you expect the ground state to look like. Add the infinite square well energy levels to your sketch.
 - (b) Carry out the variational calculation for $N=1,2,3,4$ and report your energies for the lowest three states.
 - (c) Estimate the error in your best ground state energy from (b). When you compare the energies you obtained, do they follow the pattern you expect for variational approximations?
 - (d) Plot your best ground state wave function. Does it make sense? Which infinite square well states contribute the most to it? Does this make sense?
 - (e) Treat the above potential in first order perturbation theory (for the ground state only) and compare to your results from (b). Explain whether your results make sense.
 - (f) What is the smallest N that gives the ground state energy accurate to four digits?
- (EC) What is the “exact” energy (10 digits are sufficient)? Explain why your result is exact.

Extra Credit. The best trial wave function for the helium ground state of a form like that explored in Prob. 2 utilizes an effective charge that is not constant, but rather a function of r .

- (a) Explain physically why $Z_{\text{eff}}(r)$ is better than a constant value. That is, what physics can it account for that a constant cannot.
- (b) Sketch what you think $Z_{\text{eff}}(r)$ should look like and explain its features.
- (c) Derive the equation that $Z_{\text{eff}}(r)$ must satisfy to give the best ground state value.
- (d) Solve your equation from (c) and plot your solution. Does it match what you expected from (b)?

Table 1: Exact nonrelativistic energies of two-electron atoms/ions.

Species	E_0 (a.u.)
H^-	-0.528
He	-2.904
Li^+	-7.280
Be^{2+}	-13.66
B^{3+}	-22.03
C^{4+}	-32.41