Part V
Miscellaneous items

19. SPECTROSCOPY
19.1. Group theory and symmetry
19.2. Selection rules

20. WEAK BONDS
20.1. Water

21. ADVANCED ELECTRONIC STRUCTURE
21.1. Stretched H₂, the central dilemma

Part VI
Exercises

22. ALL EXERCISES
22.1. Box with a bump down: Perturbation theory and zero-energy well-depth

Consider the potential given in Fig 6. It is of the form:

\[
v(x) = \begin{cases} 
-D, & |x| < a/4, \\ 
0, & a/4 < |x| < a/2, \\ 
\infty, & |x| > a/2. 
\end{cases}
\]  

(80)

1. For \( D = 0 \), give the energy eigenvalues and eigenfunctions. Note that the eigenfunctions may need to be shifted relative to those in a text book, because the well is centered at zero. It is also convenient to start the index at 0 instead of 1.

2. Assume \( D \) is quite small. Give an expression for the leading correction to your levels above in powers of \( D \). What is the difference between odd (first excited, third excited, etc.) and even levels, and why? Compared to what should \( D \) be small, for your approximate solution to be accurate?

3. Imagine \( D \) is very large. Give an expression for the energy levels close to the bottom of the bump. Give an estimate of the error in your expression.

4. Using the first two relevant levels in the well, write \( H \) as a 2x2 matrix and diagonalize, to obtain a different estimate of the energy of the ground state. Check this for shallow and deep wells, and comment on its accuracy.

5. Using your results above, estimate the well-depth for which the ground-state energy is exactly 0, and sketch the wavefunction.

6. Bonus: Find exact answer to previous question, and comment on accuracy of your previous answers.
22.2. Playing with units, atomic and otherwise

1. Give the atomic units of the following:
   (a) length
   (b) energy
   (c) time
   (d) speed

2. How many
   (a) eV are in a Hartree?
   (b) kcal/mol are in an eV?
   (c) kJ/mol are in a kcal/mol?
   (d) cm$^{-2}$ are in a cm$^{-1}$?
   (e) K are in a cm$^{-1}$?

3. Give the numeric values of each of the following quantities, choosing the units in which these are most conveniently reported, unless otherwise stated.
   (a) the proton rest mass in atomic units?
   (b) the speed of light in atomic units?
   (c) The largest first ionization potential of any element.
   (d) The largest electron affinity of any element.
   (e) The bond energy of H$_2$.
   (f) The vibrational frequencies of the water molecule.
   (g) The binding energy of two Ar atoms.
   (h) The Curie energy of bulk Fe.

4. What is the Hamiltonian of the He atom in atomic units? Assume an infinite mass nucleus, and ignore relativity.

5. Using the CCDB NIST chemistry database, make a table of the dissociation energies and bond lengths of all the diatomics in the first and second rows. Note any correlation between number of bonds, bond energy, and bond length.

6. Bonus question: In Problem 22.1, assume $a$ is 2Å. Give all your answers in appropriate energy units. Identify the dimensionless parameter that determines the important details of the solution.

22.3. Simple picture when bonding is asymmetric: HF

1. In our simplified picture of bonding via diagonalization of a 2x2 matrix, assuming $a$ corresponds to the electronic energy for a single H atom, what value of $\beta$ do you deduce from the $H_2$ dissociation energy?