Chem 231b, Fall 2020

Problems

(Dated: February 27, 2020)

Abstract

A collection of problems, starting from basic review of 231a, that make up the important work in Chem 231b.

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Part I

Review of basic quantum mechanics

1.   TRIAL WAVEFUNCTIONS

Given 3 standard trial wavefunctions: *[Levine 1.6,3.8]*

$$\phi_T(x) = (1 - |x|)\theta(1 - x^2) \tag{1}$$

$$\phi_G(x) = e^{-\frac{x^2}{2}} \tag{2}$$

$$\phi_E(x) = e^{-|x|} \tag{3}$$

where x is the distance in atomic units.

a) Normalize each wavefunction.

b) Calculate and plot their densities.

c) Calculate their kinetic energies from $\langle\phi| - \frac{1}{2}\frac{d^2}{dx^2}|\phi\rangle$.

d) Repeat c), using $\frac{1}{2}\int dx\,(\frac{d\phi}{dx})^2$, reconciling any differences.

e) Calculate the overlap $\langle\phi_T|\phi_E\rangle$.

f) Use your answer in e) to find a normalized basis function orthogonal to $\phi_E(x)$.

2. ONE-DIMENSIONAL HYDROGENIC ATOMS

Use atomic units and consider the potential

$$V(x) = -\delta(x)$$

[Levine 7.7]

a) For $x \neq 0$ and $x > 0$, write the general solution to the Schrödinger equation and eliminate one solution using the boundary conditions.

b) Either repeat a) for $x < 0$ or use symmetry to deduce the solution on the left.

c) Write down the jump (or cusp) condition on the wavefunction, and use it to find the eigenvalue.

d) Normalize your wavefunction.

e) Repeat problem for $V(x) = -Z\delta(x)$, where Z is the atomic number.

f) Deduce the values of $\langle \hat{T} \rangle$ and $\langle \hat{V} \rangle$ from your solutions.

3.   VARIATIONAL PRINCIPLE

Consider an electron in potential

$$V(x) = \frac{1}{2}x^2$$

[Levine 4.2]

a) Calculate $V[\phi_T] = \langle\phi_T|\frac{1}{2}x^2|\phi_T\rangle$.

b) Use your answer in a) along with $T[\phi_T]$ to extimate the ground-state energy of the oscillator. What is the error (approx $-$ exact), the % error, and why does it have its specific sign (i.e. positive or negative)?

c) Calculate % errors for T and V separately, and explain which one is larger. What is the value of T/V and what should it be?

d) Define $\phi_{T\gamma} = \sqrt{\gamma}\phi_T(\gamma x)$ where $0 < \gamma < \infty$. Either calculate or deduce $T[\phi_{T\gamma}]$.

e) Find $V[\phi_{T\gamma}]$.

f) Add your two answers to get $E[\phi_{T\gamma}]$. Plot as a function of γ and explain the shape.

g) Deduce the best value of γ and corresponding E. Is it better or worse than before? Explain.

h) Find % errors in E, T, and V, and the ration T/V. Compare with exact answer.

4. VIRIAL THEOREM

For a single particle in 1d, for any eigenstate:

$$2\langle \hat{T}\rangle = \langle x\frac{dV}{dx}\rangle$$

[Levine 14.4]

a) Show that, if $V(\gamma x) = \gamma^p V(x)$, then $2T = pV$.

b) Deduce p for the oscillator, and the ratios T/V, T/E, and V/E. Repeat for the δ well.

c) Is the virial theorem satisfied when using ϕ_T as a trial wavefunction in $\frac{1}{2}x^2$? (see variational principle problem)

d) Repeat c) when ϕ_{T_γ} is used, and γ chosen to be optimal. Does satisfaction of the virial theorem guarantee the answer is correct?

e) Give the expected ratios of energies for a quartic oscillator (x^4) and a linear well $(|x|)$.

f) Check the virial theorem for the first excited state of a harmonic oscillator.

5.   PARITY AND THE PARTICLE IN A BOX

Consider a particle in a box running from $-L/2$ to $L/2$. *[Levine 7.5]*

a) Give a formula for the eigenvalues, but label them $j = 0, 1, 2, ...$

b) Give formulas for the odd and even eigenfunctions. (You can shift the standard ones, or just find the solution that obey the new boundary conditions.)

c) Show that

$$\phi_j(-x) = (-1)^j \phi_j(x).$$

d) Without doing any calculations, say which integrals must vanish:

$$\langle 0|x|0\rangle, \ \langle 0|x|1\rangle, \ \langle 0|x^2|0\rangle, \ \langle 0|x^2|1\rangle,$$

$$\langle 0|p|0\rangle, \ \langle 0|p|1\rangle, \ \langle 0|p^2|0\rangle, \ \langle 0|p^2|1\rangle,$$

$$\langle j|x|j+1\rangle, \ \langle j+1|p|j+1\rangle,$$

e) What is the parity of the harmonic oscillator eigenstates?

f) What is the exact value of $\langle 0|x^4|1\rangle$ for a quartic oscillator?

6.   PERTURBATION THEORY AND POLARIZABILITY

Consider harmonic oscillator of frequency ω, $k = \sqrt{\omega}$ and add $\Delta V(x) = -\mathcal{E}x$. *[Levine 9.1,14.2]*

a) Show, using parity, that the change in ground state energy vanishes in first order.

b) Find the change in energy to 2nd order.

c) Use a coordinate transformation $x' = x - c$ to eliminate the linear term in

$$V(x) = -\mathcal{E}x + \frac{1}{2}kx^2$$

to get the exact energy when ΔV is turned on. Check if it agrees with b).

d) Find the change in dipole moment $\langle \psi|x|\psi \rangle = p$ to first order in ΔV. Polarizability is $\alpha = \frac{dp}{dz}$.

e) Show that $E_0 = E_0^{(0)} - \frac{1}{2}\alpha \mathcal{E}^2$.

7.   FUN WITH COMMUTATORS

[Levine 3.1]

a) Show $[A, B] = -[B, A]$.

b) Rewrite CBA in alphabetical order using $[A, B] = C$, $[B, C] = A$, and $[C, A] = B$.

c) Calculate $[x, p^2]$, $[x^2, p]$, $[p, V(x)]$.

d) Check that $\langle \psi | [\hat{H}, \hat{A}] | \psi \rangle = 0$ if ψ is an eigenstate of $\hat{H}$.

e) Use $\hat{A} = xp$ in d) to prove the virial theorem.

8. DEGENERACY AND SEPARABLE POTENTIALS

[Levine 3.5]

a) Show that if $V(\mathbf{r}) = V_x(x) + V_y(y) + V_z(z)$, then

$$E_{ijk} = E_{xi} + E_{yj} + E_{zk}$$

$$\Psi_{ijk}(\mathbf{r}) = \phi_{xi}(x)\phi_{yi}(y)\phi_{zi}(z).$$

b) Give a formula for the energy levels of a 3d cubic box of width 1 in au.

c) Give the lowest 10 energy levels and their degeneracies. Sketch the spectrum.

d) Can you estimate the energy and degeneracy of the $10,000$-th level?

e) Repeat problem for an isotropic oscillator with $\omega = 1$ in au. Combine the 3 quantum numbers into 1, and deduce a general formula for degeneracy.

9.   GAUSSIAN BASIS FUNCTIONS

Consider potential $V(x) = -\delta(x)$. *[Levine 8.5]*

a) Use $e^{-\frac{x^2}{2}}$ as a trial wavefunction to estimate ground state energy. Check virial theorem and give $\%$ errors.

b) Repeat a) but using e^{-2x^2}, i.e. with scale factor $\gamma = 2$. Deduce all expectation values rather than recalculating them. Which of these is a better trial wavefunction for this problem?

c) Now consider a linear combination of these two:

$$\phi(x) = \alpha\phi_{\mathsf{G}}(x) + \beta\phi_{\mathsf{G2}}(x)$$

Write the Hamiltonian and overlap matrices for this basis.

d) Solve the generalized eigenvalue problem to find the lowest energy solution. Give the energy and plot the wavefunction, along with $\phi_{\mathsf{G}}(x)$ and $\phi_{G2}(x)$.

e) Check variational principle is satisfied compared to answers in a) and b), and see if the virial theorem is satisfied.

f) Extra credit: Can you deduce the BEST two Gaussians for this potential?

10.   DELTA-FUNCTION IN A BOX (HARD)

Consider potential $V(x) = \lambda\delta(x)$ inside an infinite box well of width 1 centered at the origin. Estimate the ground state energy as a function of λ, for $-\infty < \lambda < \infty$. Give estimates for value of λ at which $E = 0$.

a) Give E for the three cases where you know the answer: $\lambda \to -\infty$, $\lambda = 0$, and $\lambda \to +\infty$. Sketch $E(\lambda)$ using these.

b) Use perturbation theory to find $\left.\frac{dE}{d\lambda}\right|_{\lambda=0}$ and $\left.\frac{d^2E}{d\lambda^2}\right|_{\lambda=0}$.

c) Use the ground-state wavefunction for the box as a trial wavefunction, and calculate $E_T(\lambda)$. Add to plot. Make a definite statement about the exact $E(\lambda)$. Estimate λ_0 from $E_T(\lambda)$.

d) Use the ground-state wavefunction for a box of width L $(L \leq 1)$ to improve your answer in c), repeating all parts.

e) Make a linear combination of the lowest 2 relevant levels as a basis set, and repeat c) in all parts.

f) What is your best esimate of λ_0?

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Part II

Angular momentum and the H atom

11.   LADDER OPERATORS FOR THE HARMONIC OSCILLATOR

[Levine prob 5.36] Define the raising operator

$$a^\dagger = \sqrt{\frac{\omega}{2}}\left(\hat{x} - i\frac{\hat{p}}{\omega}\right)$$

for a harmonic oscillator of frequency ω ($\hbar = m = 1$).

a) Find a, its Hermitian conjugate, the lowering operator.

b) Find their commutator, $[a, a^\dagger]$.

c) Write $\hat{H}$ in terms of a and $a^\dagger$ and constants.

d) Find $[\hat{H}, a^\dagger]$ and $[\hat{H}, a]$.

e) Use answer above to show that if $|\phi_+\rangle = a^\dagger |n\rangle$ where $\hat{H}|n\rangle = E_n |n\rangle$, then $\hat{H}|\phi_+\rangle = (E_n + \omega)|\phi_+\rangle$. Also show $|\phi_-\rangle = a|n\rangle$ has $\hat{H}|\phi_-\rangle = (E_n - \omega)|\phi_-\rangle$.

f) Since there must be a ground state $|0\rangle$, and $a|0\rangle = 0$, show $E_0 = \frac{\omega}{2}$ and by induction $E_n = (n + \frac{1}{2})\omega$.

g) Show $a^\dagger a = \hat{N}$, $a^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle$, $a|n\rangle = \sqrt{n}\,|n-1\rangle$ and writing a in differential form, check
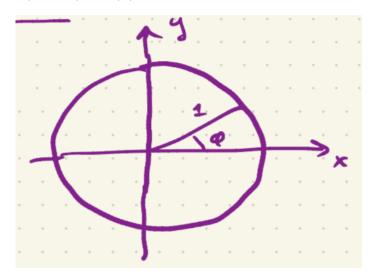
$$a\,\phi_0(x) = 0$$

is satisfied by the known solution.

h) Find $\langle 0| x |j\rangle$ and $\langle 0| x^2 |j\rangle$ without doing integrals.

i) Calculate the polarizability of the oscillator directly from perturbation theory.

j) Calculate $\langle 0| x^4 |0\rangle$ without integrals.

12. PARTICLE ON A RING

[Levine pg 105] Consider a particle on a ring of radius 1, so that $\hat{H} = -\frac{1}{2}\frac{\partial^2}{\partial\phi^2}$ and periodic boundary conditions $\psi(\phi + 2\pi) = \psi(\phi)$

a) Show that $e^{\pm ikx}$ satisfy the Schrödinger equation and $E = \frac{k^2}{2}$.

b) Show that the boundary conditions imply $k \in \mathbb{Z}$ i.e. $k = m = 0, \pm 1, , \pm 2, ...$

c) Sketch the spectrum for the first 4 energy levels, marking degeneracies.

d) Normalize your eigenfunctions, and show that they are orthogonal to each other.

e) Show that, for $m \neq 0$, the eigenfunctions can be chosen to be real and give their forms.

f) Show that your real functions are orthonormal.

13. ANGULAR MOMENTUM AND SPHERICAL HARMONICS

[Levine pg 101] Using $\mathbf{L} = \mathbf{r} \times \mathbf{p}$

a) Show (in Cartesians) $\hat{L}_x = -i(y\frac{d}{dz} - z\frac{d}{dy})$ and find $\hat{L}_y$ and $\hat{L}_z$.

b) Show $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$ and find $[\hat{L}_x, \hat{L}_z]$ and $[\hat{L}_y, \hat{L}_z]$.

c) Show $[\hat{L}^2, \hat{L}_x] = 0$ and repeat for $[\hat{L}^2, \hat{L}_y]$ and $[\hat{L}^2, \hat{L}_z]$.

d) If

$$\mathbf{L}^2 = -\hbar^2 \mathbf{\Lambda}^2$$

$$\mathbf{\Lambda}^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi^2},$$

show that

$$\hat{L}^2 Y_l^m(\Omega) = \hbar^2 l(l+1) Y_l^m(\Omega)$$

where

$$Y_l^m(\Omega) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|!)}{(l+|m|!)}} \, P_l^{|m|}(\cos\theta) \, e^{im\phi}$$

and $P_e^{|m|}(x)$ satisfy differential equations for the associated Legendre polynomials.

e) Show $\hat{L}_z Y_l^m(\Omega) = \hbar m Y_l^m(\Omega)$.

f) Defining $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$, show

$$\hat{L}_+ \hat{L}_- = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z$$

g) Show

$$\hat{L}_\pm |l, m\rangle = \sqrt{l(l+1) - m(m\pm 1)} \, |l, m\pm 1\rangle$$

h) Calculate $\langle l, m| \hat{L}_x^2 |l, m\rangle$ without doing an integral.

14.   COUPLING CONSTANT TRICK

If $\hat{H} = \hat{T} + \lambda\hat{V}$, then

$$V = \frac{dE(\lambda)}{d\lambda}\bigg|_{\lambda=1}$$

a) Check this result for the harmonic oscilator, δ-well, and even the particle in a box.

b) Show that this yields the same result as first-order perturbation theory.

c) If $\hat{H} = \hat{H}_0 + \lambda\Delta\hat{V}$, show

$$E = E_0 + \int_0^1 d\lambda \Delta V(\lambda)$$

where $\Delta V(\lambda) = \langle\psi_\lambda|\Delta\hat{V}|\psi_\lambda\rangle$ (*Hellmman-Feynman trick*).

d) Check c) for harmonic oscillator and δ-well.

15. HYDROGENIC ATOMS

[Levine chapter 6]

a) For an electron in the ground-state of an H atom, what is $\langle r \rangle$?

b) Repeat (a) for $\langle 1/r \rangle$, but do it without doing an integral. How is $1/\langle r \rangle$ related to this? Explain any similarities or differences.

c) What is the most likely distance from the nucleus at which you will find the electron?

d) Within what radius is there exactly a 90% chance of finding the electron? Make a plot of the radial distribution function, and mark all the different separations found in (a)-(d), explaining their order in terms of the shape of the plot.

e) How many nodes does a $3p_x$ orbital have, and which are angular and which are radial?

f) How much energy is needed to ionize an H atom in the 3d state?

g) Explain why there are exactly 14 f electrons.

h) What is the energy and degeneracy of the level containing the 35th excited state of H?

i) In He^+, one of the protons instantly becomes a neutron. What fraction of the electron is still in the ground state? Plot both relevant radial probability densities and rationalize your result.

j) Give a formula for transition frquencies out of the ground-state of He^+.

16. NEW TRICKS ON H ATOM

a) Sketch the spectrum of the H atom.

b) What does the virial theorem say about the relation between T and V for the H atom?

c) Use a scaled exponential with scale factor γ as a trial wavefunction for the H atom. Deduce the energy components without doing any new integrals and plot $E(\gamma)$. Show that its minimum is correct.

d) What is the best possible Gaussian with which to approximate the ground-state of the H atom, and what estimate does it give for the ground-state energy? What is the percentage error in the ionization potential estimate?

e) The cusp condition on the ground-state wavefunction for a nucleus of charge Z is

$$\Psi'(0) = -Z\,\Psi(0).$$

Check that the ground-state wavefunction of a hydrogenic atom satisfies this.

Part III

Spin statisics and many-electron atoms

17.   IDEAL FERMIONS IN A WELL

Suppose a potential $V(x)$ has exactly 4 bound states, with energies 1,2,4, and 10 eV below 0, with eigenfunctions ϕ_i, $i = 0..3$.

a) For a single electron of spin $\frac{1}{2}$, give the ground state energy, degeneracy, full wavefunction, and spin multiplicity. Sketch the energy spectrum, and give the gap and the ionization potential. List all possible transition frequencies out of this state.

b) List all possible energies in order for two ideal electrons, bound in this well. Give their terms and state their total degeneracies, and draw a spectrum up to (and a little past) the ionization potential. What is the gap, and the two ionization potentials?

c) For your answers above, draw configuration diagrams for each state, and say the level of excitation (single, double, etc.). Give the full many body wavefunction for all ground and first excited states.

d) Redraw (or relabel) your spectrum when there is a weak repulsion between the electrons, marking terms.

e) Sketch the absorption spectrum.

f) Repeat for 4 electrons, also distinguishing core from valence excitations.

18.   HE ATOM WITH EXPONENTIAL

Given $U[n] = 5\gamma/4$ in Hartree for $n(r) = 2|\phi_\gamma(r)|^2$ and $\phi(r) = exp(-r)/\sqrt{\pi}$.

a) Write down $\hat{H}$ for the He atom.

b) Write down the form of Ψ_0^{HF}, including both spatial and spin contributions.

c) Using $\phi_2(r)$ as a trial 1s orbital, calculate the one-electron energies and electron-electron repulsion. Give the ground state energy estimate, and compare with 'exact' Hartree Fock value (-79.0 eV). What is the $\%$ error in ionization potential?

d) Repeat c), but with $\phi_Z(r)$ and Z as a variational parameter. Find the optimum Z using the variational principle. Give the value of Z_{eff} and energy, and $\%$ error in ionization potential.

e) Check the virial theorem in parts c) and d).

f) Explain why $Z_{eff} \neq 2$ and the way in which it differs.

g) Repeat for 2nd ionization potential of Li. Is $\%$ error bigger or smaller? Explain.

19. ITERATION

Consider $f(x) = \frac{x^6}{6} + \frac{x^2}{2} - x + 3$

a) Deduce an equation that the position of the minimum satisfies.

Assuming you have a calculator that can take 5th roots, rewrite equation in form: $x_m = (\ldots)^{1/5}$.

b) Start with some $0 < x_m^{(0)} < 1$, iterate your equation at least 4 times. Find $f(x_m^{(0)})$ at each iteration.

c) By any means you like, find exact answer, and list errors in x_m and f_m after each iteration.

d) Repeat starting from a different x_m. Comment on the results.

e) Try starting at $x_m = 1$. What happens? How might you fix things?

f) Plot the function, marking the iteration points. Do you notice a property the function has that guarantees a minimum and makes it relatively easy to find?

20. SPECTRUM OF A NITROGEN ATOM

Study the figure of the energy level diagram of a Nitrogen atom.

Fig. 56. Energy Level Diagram for N I.

a) What is the ionization potential in Hartree, eV, kcal/mol, and wavenumbers? What is the gap (eV)?

b) How many configurations are shown? List them and give the total degeneracy of each.

c) In which configurations are Hund's rules violated?

d) Which excitations are valence (not Rydberg) excitations? Which are core excitations? Can you find any double excitations? Explain.

21. ADDITION OF ANGULAR MOMENTA

Consider two equivalent p orbitals.

a) How many angular momentum states are there in total, from the separate momenta? List the allowed values of total momentum, with their degeneracies, showing the total is the same.

b) What is the state with the largest $\mathbf{L}$, in both the separate momentum representation and the total momentum representation?

c) Use ladder operaters to step down once from the highest state to the first one down, and equate the states in one representation with the other.

d) Next, include the spins of the orbitals. How many states are possible if you ignore Pauli exclusion? If you account for it? List all the possible terms, and then the ones that are allowed.

e) Finally, writing $\mathbf{J} = \mathbf{L} + \mathbf{S}$, list the allowed J values for each term, check that you still have the same number of states.

f) For the most degenerate term, equate the highest J with corresponding L,S states, and then step down one, equating states in the two representations.

22. **HF AND KOOPMANS THEOREM**

The ground-state energy of the He atom is -79.0 eV in HF theory. The correlation energy of He is -42 mH. The eigenvalue in the HF equation is -0.918 H.

a) In Hartree, give the HF and exact ground-state energies of He. What is the percent error of the HF energy? Is the variational principle satisfied?

b) What is the HF energy for He^+? How does this compare with the exact answer?

c) Find the percent error in the HF estimate of the ionization potential. Explain difference with percent error in He energy. What does the variational principle tell you about the HF IP here?

d) Koopmans' 'theorem' says that in HF, IP is approximately equal to the absolute value of the HOMO for any electronic system. Is this approximately true here? Is it exactly true? Give the percent error of the HF HOMO as an estimate of the exact IP energy. Which is better, the IP from the energy difference or the eigenvalue?

e) If we changed from He to Li^+, do you expect your percentage error in the IP from the energy difference to get larger or smaller? Justify.

23.   BASIS SETS

Given the data set of HF calculations of the H atom and the He atom in different basis sets.

```
He+         HF      3-21G       -1.9754

He+         HF   6-311G**      -1.9981

He+         HF      STO-3G      -1.9317

He         HF   6-311G**      -2.8599

He         HF      STO-3G      -2.8078

He         HF      3-21G       -2.8357
```

a) Looking at the energies of the H atom, try to arrange the basis sets in order of size.

b) Repeat for the He atom case, and say if your answer is consistent with (a).

c) Calculate the errors in the energy due to the basis set for both H and He results.

d) Calculate the IP of He within HF in each of the given basis sets.

e) Calculate the errors in the IP results, and compare with the energy errors in (c). Explain any patterns.

f) Does the variational principle tell you anything about the basis-set error in the IP?

g) Given the actual IP of He is 24.6 eV, which basis-set gives the most accurate estimate? Why might someone say "two wrongs do not make a right"?

24. PROBLEMS FROM BERRY, RICE, AND ROSS

a) Do problems 10, 12, 14, 15, and 18 from BRR. For reference data, use the NIST website, Atomic Spectra Database. (This replaced Moore's tables, and the NBST became NIST). Also check out the Computational Chemistry Comparison and Benchmark DataBase (cccbdb) from which I got some of the basis-set results.

b) Deduce formulas for the atomic number of the noble gas atom of the n-th row, and for the width of the n-th row. Ignoring relativity, in what row would the atom with 217 electrons be and what is its ground-state configuration? What would be its lowest energy term?

c) Repeat (b) but with repulsion between electrons turned off, i.e., purely hydrogenic orbitals and energies. Just give the formula for the noble gas atoms, and state how many electrons are in the last shell of element 217, and what is the letter for the largest ang mom that might be occupied?

Part IV

Diatomics and quantum theorems

25.   BORN-OPPENHEIMER APPROXIMATION

Consider a one-dimensional world with a proton of mass m and an electron of mass 1, $m >> 1$. Let the potential be

$$V(X, x) = \frac{1}{2}(X^2 + x^2) + \frac{1}{2}(x - X)^2,$$

where X is the position of the proton, x is that of the electron.

a) Making the BO approximation, write the purely electronic Hamiltonian and, by completing the square, write its energy levels, $E_{el,n}(X)$.

b) Write the nuclear equation for the proton in the field of the electronic energy plus any other parts of the potential, to get an expression for the total energy of the system, $E_{\nu,n}$, where ν is the quantum number for proton vibrations.

c) Assuming $m = 25$, plot the lowest 12 levels, labelling them with their electronic and nuclear quantum numbers.

d) The exact solution to this problem is given by the sum of two harmonic oscillators, with frequencies

$$\omega_{\pm}^2 = 1 + \frac{1}{m} \pm \sqrt{1 - \frac{1}{m} + \frac{1}{m^2}}$$

. Show that, if $m >> 1$, this agrees with your BO solutions above.

e) Plot the exact energy levels and compare with the BO solution. Plot the errors of the BO energies as a function of energy. How accurate is BO for the lowest energy state? Does the accuracy depend on where you are in the spectrum?

f) Repeat your calculation for $m = 27$, and comment on the errors in the BO states near the first electronic excitation. In particular, comment on (near)-degeneracies.

26. H_2^+

The matrix elements in the calculation of the energy levels of H_2^+ are $S = \exp(-x)(1 + x + x^2/3)$, $h_{AA} = \gamma^2/2 - \gamma f(x)$, where $f = 1 - ((1 + x)\exp(-2x) - 1)/x$, and $h_{AB} = -\gamma^2 s/2 - \gamma(2 - \gamma)\exp(-x)(1 + x)$, where $x = \gamma * R$. Here γ is the scale factor for the 1s orbitals on each proton, separated by R.

a) Write formulas for the energy levels of the bonding and anti-bonding orbitals, $\epsilon_\pm$

b) For $\gamma = 1$, plot s, h_{AA}, and h_{AB} as a function of R. Explain their behavior as $R \to \infty$, as $R \to 0$, and their shapes.

c) Repeat previous question for $\epsilon_\pm(R)$, using your insight from those answers. Then add the nuclear repulsion and plot both energy levels. Deduce the bond length and well-depth D_e for this approximate calculation.

d) Repeat (b+c) using $\gamma = 1 + 1/2^R$, but only for the lower curve. Plot all quantities on the same plots as before, and explain all differences. Calculate bond length and depth. Compare with exact answers (google or NIST).

27. **H_2**

a) Plot the HF binding energy of H_2, approximating the Hartree energy as $U_H = \frac{5\gamma}{8}(1 + \exp(-x/4))$, using the HF energy $E = 2\epsilon + U_H/2$, and using the same optimum γ as in H_2^+.

b) Find the equilibrium bond distance and well-depth from your curve. Compare with the accurate HF values and comment.

c) Estimate the effective force constant and hence harmonic vibrational frequency and compare with exact value. Comment on what this means about the error in the shape of the curve.

d) Plot the Morse potential corresponding to H_2 on the same plot. Plot their difference near the equilibrium bond length. This would be the correlation energy if both curves were accurate. The correlation energy at equilibrium is -0.042H. Compare with the He atom. Comment on the variation of E_C with R and what this means for HF errors in bond lengths.

e) Consider your curve as $R \to \infty$. What value is it approaching? Is this correct? If not, why not? What should differ in your energy expression?

28. ANALYZING EXPERIMENTAL NUMBERS ON DIATOMIC ISOTOPES

This problem uses the first three rows of Table 7.2 of BRR. Ignore the last two columns (B and α_e) which refer to rotations. You will want to type the rest into some software, such as excel. Do all calculations in Hartree.

a) Just by staring at the numbers, can you spot two (large) typos in the table? One has a wrong digit, another has a misplaced decimal point. Correct them. Check the reduced mass results and convert into atomic units.

b) Given the results for ν_e, x_e and y_e, calculate the zero-point energy in each well.

c) Add your zero-point energies to each D_0 to estimate D_e. What should you find, and do you find it?

d) Calculate the force constant for each well. What should you find, and do you find it?

e) Using the spectroscopic formula for the energies, how many vibrational levels do you expect each well to bind?

f) Repeat (e) assuming each well was purely parabolic.

g) For H_2 only, plot the harmonic levels and the true levels.

h) Make the row of numbers for T_2.

29. THEORETICAL APPROACH TO DIATOMIC VIBRATIONS

The energy levels of a Morse potential $V_0(\exp(-2\alpha(R - R_0)) - 2\exp(-\alpha(R - R_0)))$ are

$$\epsilon_n = -V_0 \left(1 - \frac{\alpha(n + \frac{1}{2})}{\sqrt{2\,\mu\,V_0}} \right)^2 \tag{4}$$

where n takes all integer values from 0 up to where the term in brackets becomes negative, and μ is the mass.

a) Find the minimum position and well-depth, and so relate V_0 and R_0 to quantities in molecular binding curves (if they had this shape).

b) Expand the Morse potential around its minimum, and so find a formula for α in terms of the harmonic approximation to a molecular well.

c) Deduce expressions for x_e and y_e for this well, in terms of the molecular properties.

d) From your expression for x_e, find a combination of D, x_e, and ν_e that should be mass independent, and use the data to check if it is. Compare with Morse result and comment.

e) How many levels does your Morse potential predict for H_2? Compare with the perturbative answer and the harmonic approximation and comment.

f) Add the Morse levels to your plot of H_2 levels, and compare with true levels.

30.   GENERAL PROBLEMS ABOUT DIATOMICS FROM BRR

1. *Ionic bonds:* Use Table 7.3 to deduce the values of B and rho used in Eq (7.43). Are they reasonable? How might you have found them without reverse engineering? Is the agreement between calculation and experiment accurate enough by modern quantum chemistry standards? Identify which components of a KS calculation are being approximated by the separate terms in Eq(7.44).

2. *Homonuclear diatomics:* Use Fig 7.14 to identify the error in a configuration in Table 7.5. Explain the labelling of the excited states in Table 7.6.

3. *Electronegativity:* Read 7.7 and explain the spelling error in FONClBrISCHP.

4. *Potential energy surfaces:* Read 7.8 and explain the Massey criterion. When can curves cross and when do they not? If curves do not cross, can molecules change PES?

5. *Hydrides and isoelectronic series:* Read 7.9 and explain what is special about diatomic hydrides. Explain how hydrogen bonding upsets trends in boiling point data. Do problem 7.20.

Part V

Electronic stucture theory

31.   PARTICLES IN A BOX VIA DFT

a) Write down the exact energies of the first three levels of the particle in a box of length 1, the sums of these energies for 1, 2, and 3 levels, plot the wavefunctions for each level, and plot the densities for 1, 2, and 3 same-spin fermions in the box.

b) Solve the Euler-Lagrange equation with the TF approximation to the kinetic energy to find the relation between N and μ. Solve for the mininimizing density, and plot it on your density plots. Comment on the errors made by this approximate density, and how the error behaves as N grows. Calculate the integral of $n^2(x)$ for $N = 1, 2, 3$, both exactly and approximately and comment as N grows.

c) Make a table of the exact and approximate kinetic energies for each N and report the percentage error. Comment on the absolute error and percent error as N grows.

d) Now calculate the TF kinetic energy on the exact densities and add the results to the table, including errors and comment as N grows. What do you conclude is the main source of error in the self-consistent TF calculation?

e) Remake your table to report eigenvalues, by calculating the difference between having N and $N-1$ particles in the box, and calculate errors for both self-consistent TF and TF on exact densities.

f) Deduce formulas for E_N for the exact and two approximate sets of numbers, and then add $N = 100$ to your table. What aspect of the formulas show that TF becomes relatively exact as N gets large? (Hint: In every case, the formulas are cubic polynomials in N with no constant term (why?) whose coefficients could be found by fitting to 3 values of N.)

32. HARMONIC OSCILLATORS IN DFT

a) For the harmonic oscillator $v(x) = x^2/2$, write the formula for the TF density in terms of μ.

b) By doing the integral between the turning points, find a formula for N as a function of μ.

c) Get formulas for T_N and E_N.

d) By subtracting $N - 1$ from N, deduce a formula for the N-th energy level. What is its error?

e) For $N = 1, 2, 3$, plot both the exact and the approximate densities of the harmonic well. Why would the phrase "getting the right answer for the wrong reason" come to mind?

f) Calculate the integral of $n^2(x)$ for $N = 1, 2, 3$ both exactly and approximately and comment on trends of errors with N.

33. MORSE OSCILLATORS IN DFT

a) For the Morse potential given for the diatomics problem,

$$E_N^{TF} = -NV_0(1 - y + y^2/3)$$

where $y = N/\alpha$. Deduce a formula for individual eigenvalues.

b) For your parameters for H_2 modelled as a Morse potential. list the exact and approximate vibrational energy levels. Comment on where the largest errors are.

c) What happens for D_2? Does the TF result do better or worse than in H_2? Does it depend on which eigenvalues you look at? Why does it get better or worse?