Problem Set 10

1. Infrared Spectroscopy. Simple linear spectroscopy transition moments (i.e. how strong an absorption is) can be calculated from the dipole operator:

$$\langle \psi_f | -e \cdot \hat{d} | \psi_i \rangle = -e \cdot \int \psi_f \cdot d \cdot \psi_i \cdot \partial \tau$$

where $\hat{d} = \hat{x}, \hat{y}$, or $\hat{z}$ depending on the polarization of the incident radiation, ψ_f is the final state of the molecule after absorption and ψ_i is the initial state. In the case of vibrational spectroscopy, a bond vibration can be assumed to be 1D (along x), and the wavefunctions are harmonic oscillator wavefunctions represented by $|n\rangle, n = 0,1,2 ...,$ where n is an integer that corresponds to the ground ($n = 0$) or excited states ($n > 0$).

For this question, create a matrix representation of $-e \cdot \hat{d} = -e \cdot \hat{x}$ in the $|n\rangle$ basis for $n = 0,1,2,3$ (otherwise the matrix will be infinite) to:

a) Determine a selection rule for vibrational transitions.

b) Please explain an observation I made as a graduate student (Snee et al., J. Am. Chem. Soc. **2002**, *124*, 35, 10605–10612, data shown here). In this time resolved UV-pump IR-probe study, after UV excitation of CpRh(CO)₃ and photo-ejection of a CO ligand in a heptane solvent a vibrational "hot band" of the CO stretch of the CpRh(CO)₂ product was observed in the time resolved IR
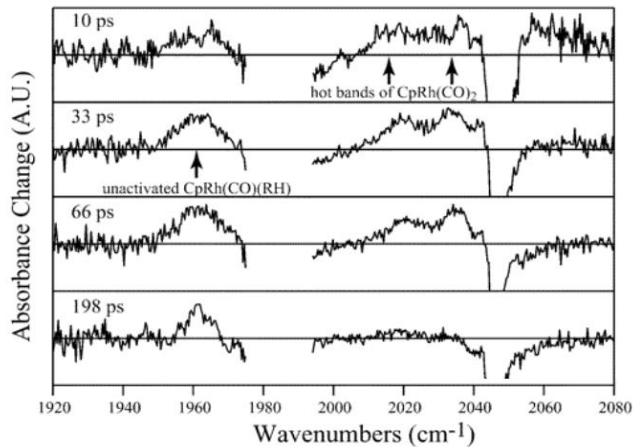
spectra. These "hot bands" correspond to CO's $|3\rangle \leftarrow |2\rangle$ transition at 2020 cm⁻¹ and $|2\rangle \leftarrow |1\rangle$ at 2030 cm⁻¹, while the ground state $|1\rangle \leftarrow |0\rangle$ transition appears as a "parent bleach" signal at 2045 cm⁻¹. The red-shift in energy is due to the anharmonicity of the CO ligand (not important to this question). These transitions were due to vibrational excitation of the product with leftover energy from the UV pump, and they disappear after ~200 ps due to vibrational relaxation.

Here is the question- the intensities of these hot band absorptions were very strong, much more than I expected! Does the matrix representation of $|\langle -e \cdot \hat{x} \rangle|^2$ help explain this observation?

Identities: $\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i\hat{p}}{m\omega} \right)$ $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$

$\hat{a}^+ = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i\hat{p}}{m\omega} \right)$ $\hat{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle$

2. Finite Difference Method. Let's say we wanted to develop a 5-point stencil for the Finite Difference method:

$$f(x)' = a \cdot f(x - 2h) + b \cdot f(x - h) + c \cdot f(x) + d \cdot f(x + h) + e \cdot f(x + 2h)$$

and

$$f(x)'' = a \cdot f(x - 2h) + b \cdot f(x - h) + c \cdot f(x) + d \cdot f(x + h) + e \cdot f(x + 2h)$$

Please determine the coefficients a,b,c,d and e for $f(x)'$ and $f(x)''$. **Hint:** use Matlab and note that in the 3-point stencil example there are three equations for solving the three unknowns. How will you generate 5 equations to solve for 5 unknowns?

3. Finite Difference Method: Core/shell quantum dots such as CdSe/CdS have a CdSe core, a CdS shell, and then organic ligands on the surface. Please plot the first three eigenstates of an electron in a 3 nm core CdSe quantum dot with a 2 nm thick CdS shell using a 3-point stencil. Also show the ground and next 9 excited state energies in units of eV.

a) Please send your energies, first three wavefunctions and code so I can see if you modeled the QD correctly. Note that you may or may not need to "flip" up a wavefunction.

b) Does the inclusion of a shell increase or decrease the ground state energy of the electron? (hint: need to solve the energy for the "core only" problem, for which you could simply set the shell potential energy to the organic ligand potential energy of 3 eV).

c) Why do you think there is a kink in the energy diagram starting at the 7th state?

When you attempt to answer this question, you need these data:
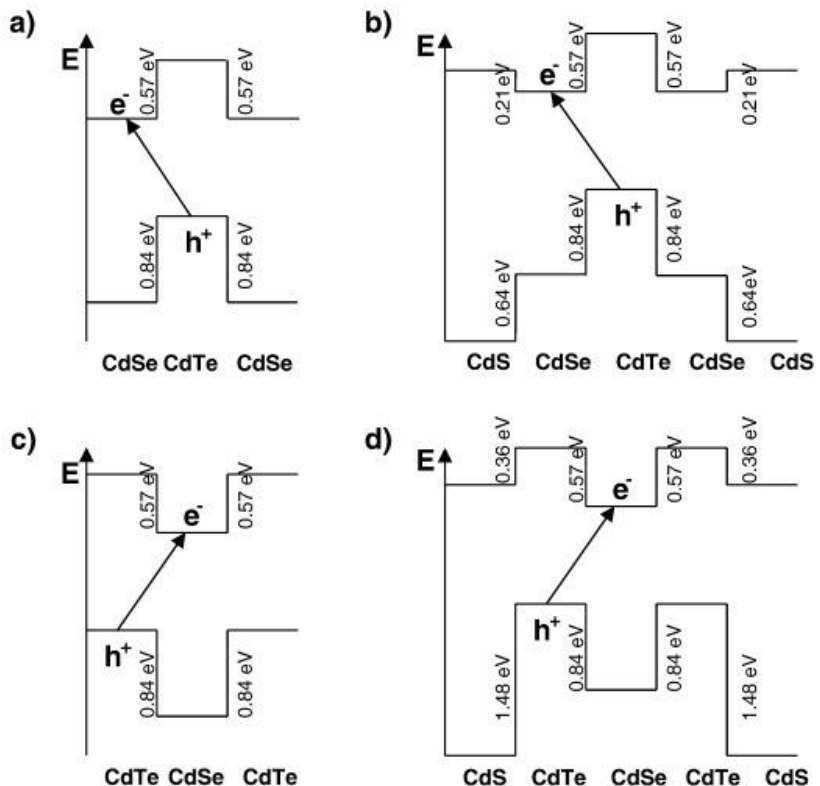
Mass of an electron in CdSe: 0.13 m_e
Mass of an electron in CdS: 0.21 m_e
You have to model the electron's potential energy increasing from the CdSe core to the shell (you can assume V(r)=0 for the CdSe core). Here is a band offset diagram I pulled off Google:

a)
CdSe CdTe CdSe

b)
CdS CdSe CdTe CdSe CdS

c)
CdTe CdSe CdTe

d)
CdS CdTe CdSe CdTe CdS

Last, you can assume that outside the CdS shell the electron experiences a +3.0 eV barrier.

Note, the way that electronic structure works using the "effective mass approximation" is to assume that excitation of a semiconductor results in an electron in the conduction band, and a fictitious particle called a "hole" in the valence band. The hole is basically a negative electron, its job is to represent the absence of the electron in the valence. This theory works quite well so long as you scale the masses of the electron and valence to match experimentally derived data. Last hint- when you add an inorganic shell to the core, the emission is red-shifted (i.e. lower in energy).

4. Split Operator. For this problem please create a potential energy surface and calculate the ground and excited state wavefunctions.

An example code is provided that does the harmonic oscillator problem; you have to modify it to change the potential surface. I suggest one of the following:
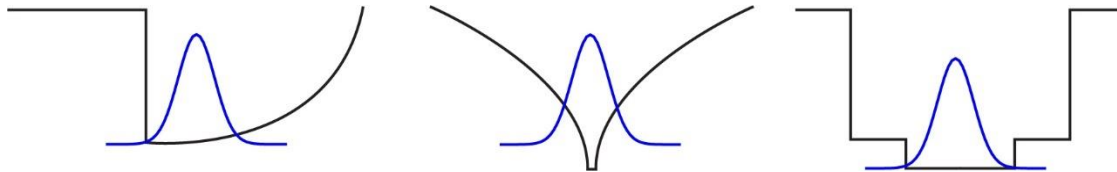
For this question:

a) Please provide a spectrum of the energies and calculate the energies of the ground and 1st excited state.

b) Please provide the calculated ground and 1st excited state wavefunctions.

Hint: You have to be careful where you start the wavefunction on the PES. If you have a very bad starting wavefunction on an unrealistic PES the calculation will go haywire. Also, your answers will have both real and imaginary components; it's basically impossible to avoid this so show both (or you can show the absolute value). In that regard, no matter what your PES the ground and excited states should look something like this diagram, in that generally a ground state has no nodes yet the 1st excited state has one.
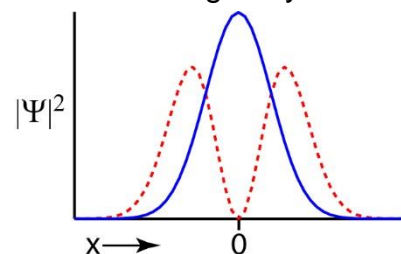
5. Visualizing Wavefunctions with the Split Operator Method. Let's make a video! Not of the kitties, but of a wavefunction on the potential energy surface that you used in question 4. Use the split operator method to visualize a wavefunction over time and integrate the following code to make a video of the motion. You should do the following:

a) Make a video using the ground state eigenfunction as the starting wavefunction.

b) Displace that wavefunction and rerun the dynamics. What is different in this case? Can you relate what you see to some of our lessons about the time evolution of Hamiltonian eigenstates?

I have included a short script in the example to help you along. Please send me the video.

6. Angular Momentum Addition: Consider a carbon atom with 2 unpaired p-electrons. We showed in class that the term symbols are $^1D_2$ (five states), $^3P_2$ (five of states), $^3P_1$ (three states), $^3P_0$ (one state) and $^1S_0$ (one state), for a total of 15. Problem- when I look at the electron configurations, I see 6 states with $m_s=\pm1$; these are clearly triplet states:

Likewise, the three configurations that are doubly occupied must be singlets:

Since I should have 9 triplet states and 6 singlets, we seem to be missing three of each! They all must be somewhere in these 6 states, but they all seem to be singlets because $m_s=0$ for each of them:

Here is the actual question- According to the [Clebsch-Gordan table](#), the $^3P_0$ state should be:

$$^3P_0 = \sqrt{\frac{1}{3}}\,|+1,-1\rangle - \sqrt{\frac{1}{3}}\,|0,0\rangle + \sqrt{\frac{1}{3}}\,|-1,+1\rangle$$

and the $^1D_2$ state should be:

$$^1D_2 = |0,0\rangle$$

?

The problem with the $|0,0\rangle$ is that there are two of them in the 6 basis states identified above:

Normally I would think that one is triplet (belongs to $^3P_0$) and the other is singlet (belongs to $^1D_2$), but they are basically the same except for the electrons being flipped over! It doesn't seem possible to distinguish one of them as triplet and the other singlet! Please resolve the problem and write out the correct wavefunctions for the states in terms of the basis functions. *Hint:* the answer is stupid-simple.

7. Term Symbol: A nitrogen atom has three unpaired 2p electrons.

a) What are the possible term symbols? Please start with the provided table of electron configurations and then determine the patterns inside of them to know what the terms

are. Hint: I'm sure you can already look up that the ground state is $^4S_{3/2}$, too bad there are two other terms!

b) Can you use the Clebsch-Gordan table to identify which single basis state gives rise to the $^2D_{5/2}$ state? Specifically I am looking for the J=5/2, M_J=+5/2, because there are technically 6 different J=5/2 states (M_J=5/2, 3/2, 1/2, -1/2, -3/2, -5/2). ***Hint:*** This question is easy because it is just one of the basis states, whereas the others are linear combinations.

Appendix: Example MATLAB codes

Finite Difference Method. Calculation of the 3-point stencil constants for a 1st derivative:

```
syms a b c;
eqn1 = a + b + c == 0;
eqn2 = -h*a + h*c == 1;
eqn3 = 1/2*h^2*a + 1/2*h^2*c == 0;
[A,B] = equationsToMatrix([eqn1, eqn2, eqn3], [a, b, c]);
der = linsolve(A,B)

der =
  -1/(2*h)
        0
   1/(2*h)
```

Finite Difference Method. Example code for a 0.5 m_e particle in a 3 nm sphere using a 3-point stencil:

```matlab
clear all; close all;
lengsim=1000; %Wavefunction has 1000 grid points
delr=0.2;      %grid spacing
delrsq=delr*delr;
radius=56.7;   %This is in Bohrs, corresponds to 3 nm.
hbar=1;        %atomic units afterall
me=0.5;        %the particle has half and electron's mass
constants=-hbar/2/me; %p^2 operator's constants

for j=1:lengsim      %This is here to initialize the sim
    r(j)=j*delr;     %Defines the grid
    VR(j)=0;         %the potential energy
    if (r(j)>radius) %if the particel is >3 nm, the potential is high!
        VR(j)=100;   %100 Hartree is an extremely high energy.
    end;
end;
%The 1st line of the Finite Diff matrix
H(1,1)=constants*(-2/delrsq)+VR(1);
H(1,2)=constants*(1/delrsq+2/r(1)*1/2/delr);

for j=2:lengsim
    H(j,j)=constants*(-2/delrsq)+VR(j);
    H(j,j+1)=constants*(1/delrsq+2/r(j)*1/2/delr);
    H(j,j-1)=constants*(1/delrsq-2/r(j)*1/2/delr);
end;

[Psi,D]=eigs(sparse(H(1:lengsim,1:lengsim)),10,0);
%Matlab's calculation of eigenvalues etc.

for i=1:10
    energies(i)=D(i,i);
end;
plot(r*0.0529,-Psi(:,1)/sqrt(sum(Psi(:,1).*Psi(:,1).*r'.*r')));
hold on;
plot(r*0.0529,-Psi(:,2)/sqrt(sum(Psi(:,2).*Psi(:,2).*r'.*r')));
plot(r*0.0529,-Psi(:,3)/sqrt(sum(Psi(:,3).*Psi(:,3).*r'.*r')));
title('First three normalized s-state wavefunctions')
figure;
plot(energies(1:10),'bo'); title('Energies')
```

Split Operator. Example code for an excited CO molecule a harmonic potential. This code also creates a video of the process:

```matlab
clear all;
vido = VideoWriter('chem542.avi'); % Matlab specific commands
open(vido);            % Matlab specific video writer
dx=0.005;              % Grid spacing, in units of Bohr
mass=1.138e-27;        % Reduced mass of CO in kg
mass=mass/9.109e-31    % Now in units of electron mass
kf=1860;               %Spring constant, in N/m
kf=kf*1.214e7*5.29e-11; % Spring constant, in Hartree/Bohr
energy1=0.5*sqrt(kf/mass); % Energy of the ground state
energy2=1.5*sqrt(kf/mass); % Energy of the 1st excited state
dt=0.005;                  % Time constant, 1 unit is ~2.42e-17 sec
L=2^12;                % Number of grid points, ~1000
```

```matlab
tott=50000;                % Number of time steps
boxlength=L*dx;            % Length of the side of a box in Bohrs
norm=0;                    % For normalizing the wavefunction
i=sqrt(-1);
for x=1:L
  eigen1(x)=0.0;                       %for calculating the ground state
  eigen2(x)=0.0;                       %for the 1st excited state
  x2(x)=x*dx-boxlength/2;                 %center the grid
  length=sqrt(x2(x)^2);                   %distance from the center
  wf(x)=exp(-sqrt(kf*mass)/2*(length+0.50)^2);
  %+10*x2*exp(-sqrt(kf*mass)/2*length^2); %initialize the w.f.
  potential(x)=0.5*kf*length^2;          %harmonic oscillator potential
  V(x)=exp(-sqrt(-1)*dt*potential(x)); %V operator
  norm=norm+wf(x)*conj(wf(x)); %for normalizing the w.f.
  mx3=x;                               %Part of momentum operator
  if(x>L/2)
    mx3=L-x;                           %Part of the momentum operator
  end;
  mx2=mx3*2.0*pi/boxlength;           %Part of the momentum operator
  K(x)=exp(-i*dt/4.0/mass*mx2*mx2); %The momentum operator
end;
wf=wf/sqrt(norm);                     %Norm the wavefunction
wf_initial=wf;                        %Save the wf for furhter calculations
plot(x2,abs(wf));                       %1st frame of the movie!
hold on;
plot(x2,potential/2,'r');
axis([-1 1 -.01 0.35]);
frame = getframe(gcf);
writeVideo(vido,frame);
clf(figure(1));
wf=fft(wf);                           %Fourier Transform for K operator
for t=1:tott
    wf=K.*wf;
    wf=ifft(wf);
    wf=V.*wf;
    cor(t)=real(sum(sum(sum(wf_initial.*wf))))+i*imag(sum(sum(sum(wf_initial.*wf))));
    eigen1=eigen1+exp(sqrt(-1)*energy1*t*dt).*wf;
    eigen2=eigen2+exp(sqrt(-1)*energy2*t*dt).*wf;
    if (mod(t,25)==0)                 %Don't video image every frame
      plot(x2,abs(wf));
      hold on;
      plot(x2,potential/2,'r');
      axis([-1 1 -0.01 0.35]);
      frame = getframe(gcf);
      writeVideo(vido,frame);
      clf(figure(1));
    end;
    wf=fft(wf);
    wf=K.*wf;
end;


close(vido);
```

Here are the potential configurations of a nitrogen atom for question 6a:

$m_l=1$	$m_l=0$	$m_l=-1$	M_L	M_S
↑	↑	↑	0	+3/2
↓	↓	↓	0	-3/2
↕	↑	↑	0	+1/2
↑	↕	↑	0	+1/2
↑	↑	↕	0	+1/2
↑	↕	↕	0	-1/2
↓	↑	↕	0	-1/2
↓	↓	↑	0	-1/2
↑↓	↑	—	+2	+1/2
↑↓	—	↑	+1	+1/2
↑↓	↓	—	+2	-1/2
↑↓	—	↓	+1	-1/2
↑	↑↓	—	+1	+1/2
—	↑↓	↑	-1	+1/2
↓	↑↓	—	+1	-1/2
—	↑↓	↓	-1	-1/2
↑	—	↑↓	-1	+1/2
—	↑	↑↓	-2	+1/2
↓	—	↑↓	-1	-1/2
—	↓	↑↓	-2	-1/2