5.73

EXAM 1

NAME: _____

You may discuss what the questions mean with each other, but you may not discuss strategies for solving the problems with each other. You may obtain a computer program from another member of the class, but you must credit that person for providing the program. I will answer email questions and, if appropriate, copy the entire class with the question and my response.

You have used all of the computer programs you will need for this exam on problem sets #1 – 5.

If you find that you cannot solve one or more of the parts of this exam, please try to simplify the problem so that it becomes one you can solve. If this simplification is not possible, please describe what you *expect* to find. All insights will be richly rewarded.

GRADING:

A.	/10
B.	/15
C.	/15
D.	/10
E.	/10
F.	/20
G.	/10
H.	/10

TOTAL: /100

The two potential energy curves on which this entire exam is based are

$V_1(x) = a|x|$ (a in erg·cm^{-1}, x in cm)
$V_2(x) = -a\,(x - 2\times10^{-7}\text{ cm})$ $\quad x < 2\times10^{-7}$ cm
$V_2(x) = 0$ $\quad 2\times10^{-7}\text{ cm} \le x \le 11\times10^{-7}$ L (L in cm)
$V_2(x) = \infty$ $\quad x > 11\times10^{-7}$L
L = 1 cm (The limit L $\to \infty$ will be examined in one question).

A. (10 points) Compute the first 10 eigen-energies $\left(E_0^1 - E_9^1\right)$ of the Hamiltonian for $V_1(x)$,

$$\mathbf{H}_1 = \mathbf{p}^2/2m + V_1(x)$$

and *save the eigenfunctions*. Adjust m and a so that the 5th level (i.e., the one with 4 internal nodes) lies at $E = ax_{\pm}(E)$ where

$$x_{\pm}(E) = \pm1\times10^{-7}\text{ cm}.$$

The best way to solve this problem is the exact analytic solution based on zeroes of Airy functions and derivatives of Airy functions. This permits an exact value of the parameter a to be obtained (assuming a value of m).

B. (15 points) Compute $\psi(x)$ and the density of states, $\rho(E)$, for each of the 10 eigenstates of the Hamiltonian for V_2, $\mathbf{H}_2$, for L = 1cm

$$\mathbf{H}_2 = \mathbf{p}^2/2m + V_2(x)$$

that have energies nearest those of the lowest 10 eigenstates of $\mathbf{H}_1$. (Note that there will be *at least* 50 eigenstates of $\mathbf{H}_2$ at $E \le E_9^1$. You are looking for 10 pairs of near-degenerate eigenstates, one member of the pair from $\mathbf{H}_1$, the other from $\mathbf{H}_2$).
[**HINT**: If you use DVR to find the energies and eigenfunctions of $\mathbf{H}_2$, I suggest you convert $V_2(x)$ into a symmetric potential centered at $x = 11\times10^{-7}$ cm and retain the left half of only the (re-normalized) odd-symmetry eigenstates.]

The best way to find the energies of $\mathbf{H}_2$ is by Numerov-Cooley. The best way to obtain the density of states is by the WKB quantization condition converted to dn/dE form. The WKB method is especially well suited to taking the limit L $\to \infty$. The simple numerical procedure

$$\rho(E_n) = \frac{1}{E_n - E_{n-1}} \quad \text{or} \quad = \frac{1}{2}\left[\frac{1}{E_n - E_{n-1}} + \frac{1}{E_{n+1} - E_n}\right]$$

works well for part B and agrees with WKB. DVR has the disadvantage that you still need to import the analytic harmonic oscillator eigenfunctions in order to use your DVR eigenvectors to compute overlap integrals in subsequent parts.

C. (15 points) Compute the overlap integral, $\langle n_1|n_2\rangle$, and the "*x*-centroid", $\bar{x}_{n_1 n_2}$, $\langle n_1|x|n_2\rangle / \langle n_1|n_2\rangle$, for each of the 10 n_1, n_2 near degenerate pairs of eigenstates.

(*i*) What does the qualitative structure of E vs. $\langle n_1|n2\rangle$ tell you?
(*ii*) Compare the values of the *x*-centroids to the value of *x* at which $V_1(x)$ and $V_2(x)$ intersect. What does this tell you and what does "stationary phase" have to do with your observation?

The overlap and $\langle n_1|x|n_2\rangle$ integrals both accumulate in the vicinity of the stationary phase point <u>for the integrand</u>, which is located very near the x-value of the intersection of the two potentials, x_c. Because the two wavefunctions have the same classical momentum at x_c, the $\psi_1^* \psi_2$ integrand stops oscillating in the neighborhood of x_c. The length of the stationary phase region is determined by the difference between the derivatives of $V_1(x)$ and $V_2(x)$ at x_c. This determines the range about x_c where ψ_1 and ψ_2 develop $\pi/2$ phase difference.
The values of the $\langle n_1|n_2\rangle$ and $\langle n_1|x|n_2\rangle$ integrals are determined by 3 factors:

(i) The classical $p^{-1/2}(x)$ envelope at x_c.

(ii) The length of the stationary phase region (determined by $\frac{dV_1}{dx} - \frac{dV_2}{dx}$ at $x = x_c$).

(iii) The phase of ψ_1 relative to that of ψ_2 at x_c. If one wavefunction has a node and the other has an antinode at x_c, then the overlap will be accidentally close to 0.

(See handout from my book, pages 279-285.)

The structure of E vs. $\langle n_1|n_2\rangle$ gives you the energy at which $V_1(x)$ crosses $V_2(x)$ from the initial turning-on of the overlap. Since you do not initially know the strength of the interaction, you can't use the actual measured quantitative effect of the interaction to determine anything about the shapes of the potentials beyond the fact that they intersect at $E = V_1(x_c) = V_2(x_c)$. However, the oscillatory structure of $\langle n_1|n_2\rangle$ does give you an experimental sample of $\frac{dV_1}{dx} - \frac{dV_2}{dx}$ at x_c. This information is encoded in the oscillatory structure (period of oscillation, relative magnitudes of successive maxima) of $\langle n_1|n_2\rangle$.

The x-centroid is not a measurable quantity. However, its constant value of x_c is a simple consequence of stationary phase. Both $\langle n_1|x|n_2\rangle$ and $\langle n_1|n_2\rangle$ accumulate in the vicinity of x_c. The relative phase effects (in comment (iii) above) are the same for both integrals and cancel in the definition of the x-centroid. The fact that $\frac{\langle n_1|x|n_2\rangle}{\langle n_1|n_2\rangle} = x_c$ means that observable quantities sample inter-state interaction functions exclusively at the x_c values of the curve crossings. Convenient for experimentalists but sad news for theorists!

D. (10 points) In part **B** you computed the density of "box-normalized" states, $\rho_L(E)$, for $\mathbf{H}_2$. Convert to the density of states for continuum functions normalized to a δ–function in E, using

$$\rho_{\delta E}(E) = \lim_{L=\infty}\left[\frac{1}{L}\rho_L(E)\right]$$

You may use WKB quantization or any convenient shortcut to obtain $\rho_{\delta E}(E)$ for $\mathbf{H}_2$.

The best way to solve for $\rho_{\delta E}(E)$ is to use the density of states derived from WKB quantization. Trial and error increases of L give the same result, but in a cumbersome and E-dependent manner. One really interesting result is that the $L \to \infty$ limit gives the density of states for a free particle. Why? Because the region of x where V(x) is x-dependent is vastly smaller than the region of x where V(x) = constant!

E. (10 points) Fermi's Golden Rule, for the decay rate of a bound state embedded in a continuum, is

$$\frac{1}{\tau} = \frac{2\pi}{\hbar}\left|\langle f|\mathbf{H}|i,E_i\rangle\right|^2 \rho_f(E_i)$$

where $1/\tau$ is the decay rate (τ is the lifetime, as in $e^{-t/\tau}$), $\langle f|$ is the final state normalized to a δ-function in E at $E = E_i$, $|i,E_i\rangle$ is the box-normalized initial state that belongs to the E_i eigen-energy, and $\rho_f(E_i)$ is the δ-function normalized final state density at $E = E_i$. This equation describes the rate of decay of population prepared at t = 0 in the stationary eigenstate E_i that results from the interaction between the discrete and continuum states at $E = E_i$. Compute τ for each of the 10 lowest levels of $\mathbf{H}_1$, where

$\mathbf{H}_{12} = \langle n_1|A(x)|n_2\rangle$

and

$$A(x) = A(0) + \left.\frac{dA}{dx}\right|_{x=0} \mathbf{x}$$

thus

$$\mathbf{H}_{n_1 n_2} = \langle n_1 | n_2 \rangle \left[A(0) + \left.\frac{dA}{dx}\right|_{x=0} \bar{x}_{n_1 n_2} \right].$$

Let $A(0) = 0.1a$ and $\left.\frac{dA}{dx}\right|_{x=0} = 0.1a.$

Note that A(x) is exclusively sampled at $x = 1 \times 10^{-7}$ cm and that there is no good experimental way to distinguish between A(x) = constant and A(x) linear in x. (You determined a value for a in part **A**.)

To use the Fermi Golden Rule formula, it is essential that you use the final state density, $\rho_f(E)$, that is appropriate for the way the final continuum states are normalized: box vs. δ-function in E. Note that as $L \rightarrow \infty$ the $\langle n_1|n_2\rangle^2$ overlap integral squared (box normalized) goes as 1/L but ρ_f goes as L. The two L-dependences cancel, at least they cancel once L is large enough. It is large enough when L is large enough. When the energy of the continuum state is so close to that of the bound state that the phase error at x_c (discussed in the comment about part **C**) is negligible.

The form of the interaction function illustrates the "x-centroid approximation." A(x) is sampled exclusively at x_c. For the values given

$$\mathbf{H}_{n_1 n_2} = \langle n_1 \,|\, n_2 \rangle \; a\,(0.1).$$

F. (20 points) Solve for the eigen-energies of the total **H**

$$\mathbf{H} = \begin{pmatrix} E(n_1 = 0) & 0 & \langle n_1 | A(x) | n_2 \rangle \\ 0 & E(n_1 = 9) & \\ \hline & & E(n_2 = 0) \\ sym & & 0 \\ & & 0 \quad E(n_2 = \max) \end{pmatrix}$$

where the upper left-hand block is the diagonal $\mathbf{H}_1$, the lower right-hand block is the diagonal $\mathbf{H}_2$ (with L = 1cm), and the $\mathbf{H}_{12}$ off-diagonal block couples the eigenstates of $\mathbf{H}_1$ and $\mathbf{H}_2$ and is filled with an enormous number of off-diagonal matrix elements of the form $\langle n_1|n_2\rangle$ 2A(0). You have two choices for filling the elements of $\mathbf{H}_{12}$. The hard choice is to compute all of the $n_1 = 0–9$, $n_2 = 0–n_{max}$ overlap integrals. The easy choice is to fill $\mathbf{H}_{12}$ with random numbers chosen so that, for each value of n_1, their root mean squared value is equal to 2A(0) $\langle n_1 = n | n_2' \rangle$, where v_2' is the quantum number for the level of $\mathbf{H}_2$ most nearly degenerate with the *n*-th level of $\mathbf{H}_1$. Number the eigen-energies of the total **H** in order of increasing E and plot $\frac{1}{E_{n+1} - E_n}$ vs. E_n. This is the discretized density of states. You should see "resonances" in the density of states centered at the eigen-energies of $\mathbf{H}_1$ and with full width at half maximum (FWHM) equal to something like $\hbar/\tau$, where the τ values are what you computed in part **E**. It is possible that, for L = 1 cm, the density of states in **H** is too sparse to capture a sufficient number of points on the Lorentzian shape $\rho(E)$ at each of the 10 resonances.

Fermi's Golden Rule (FGR) is more accurately expressed in terms of the average of the squared matrix element at E. This is why I told you that you could take a shortcut and replace the actual $\langle n_1|n_2\rangle$ matrix elements by random numbers slaved to the value for the pair of near degenerate levels from $V_1(x)$ and $V_2(x)$. It is most accurate to use for $\rho(E)$

$$\rho(E) \approx \frac{1}{2}\left[\frac{1}{E_n - E_{n-1}} + \frac{1}{E_{n+1} - E_n}\right]$$

because this partly corrects for accidental near degeneracies and makes the resonances more symmetric (as they really should be).

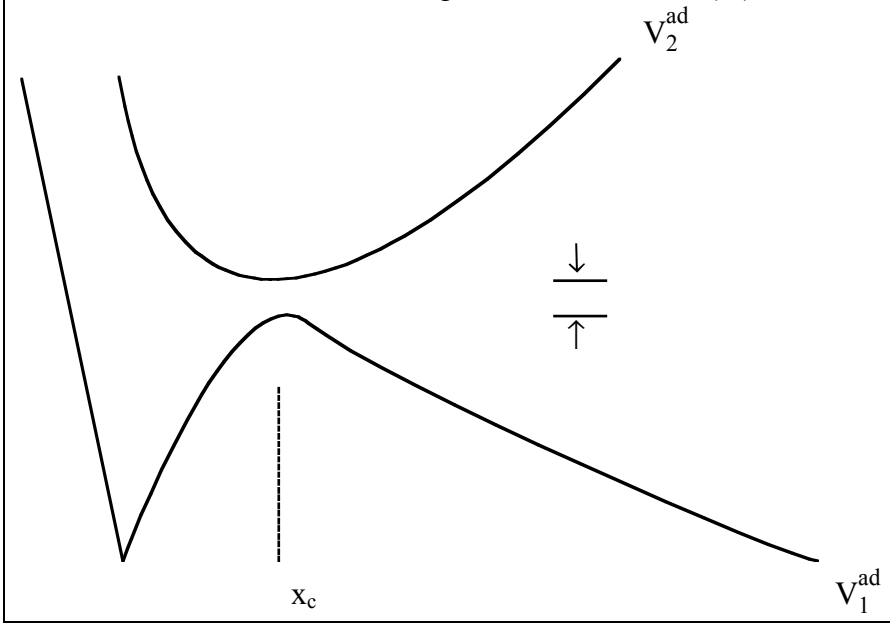
G. (10 points) Explore the effects of A(0) and/or L on the shape of the 5th and 6th resonances (the ones just at and just above the intersection between $V_1(x)$ and $V_2(x)$).

Increasing A(0) should make the resonances broader, precisely as required by the FGR. Increasing L will do nothing at all, because of the canceling effects on $|\langle n_1|n_2\rangle|^2$ and $\rho_L(x)$.

H. (10 points) The qualitative behavior you have observed in the decay rates and widths of the quasi-eigenstates that arise from the interaction between a bound state and a continuum provides experimental signatures for the energy of the intersection between V_1 and V_2 and for the difference in the derivatives, $\left(\frac{dV_1}{dx} - \frac{dV_2}{dx}\right)$, evaluated at the x coordinate of the intersection. What are these signatures?

See the comment for part **C**. The most dramatic thing is the sudden turning on of the interaction (predissociation) just above the energy of the curve crossing. The oscillations of the resonance widths give information about $\frac{dV_1}{dx}$ and $\frac{dV_2}{dx}$ at x_c.

There is an entirely different way to look at these effects, and that is the "Landau-Zener" picture. The two crossing potentials (called "diabatic") are converted to "adiabatic" potentials by diagonalizing **H** at each x. One gets two adiabatic potentials that do not cross, but approach to each other most closely at $x = x_c$. The vertical energy difference between the adiabatic potentials at x_c is $2A(x_c)$.



Now the picture becomes more classical. If the particle, initially on V_1^{ad} at $E > V_2^{ad}$ (x_c), is moving fast toward larger x in the region of x_c, it does not notice the avoided crossing and jumps from V_1^{ad} to V_2^{ad} and remains bound. However, if the particle is moving slowly near x_c, it follows the adiabatic curve and dissociates. This would be a good problem for an exam in 5.74!

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