Quantum Physics III (8.06) Spring 2005
Solution Set 7

April 5, 2005

1. **Variational bound on the ground state in an exponential potential (12 points)**

(Full credit will be given to answers to this problem that set $\hbar = 1$.)

(a) **(1 point)** The condition that the wave function be normalized yields $1 = \int d^3x\, C^2\, e^{-2\lambda r} = 4\pi C^2 \int dr\, r^2 e^{-2\lambda r}$. Defining $x = 2\lambda r$, we find $1 = 4\pi C^2 (\frac{1}{2\lambda})^3 \int dx\, x^2 e^{-x}$. Using the identity $\int_0^\infty dx\, x^2 e^{-x} = 2$, we find

$$C^2 = \frac{\lambda^3}{\pi}.$$

(b) **(2 points)** Our trial wavefunction has only radial dependence, therefore angular parts in kintetic energy give 0 when they act on the wavefunction. It is sensible to choose an s-wave ansatz, as was given in the problem, since we expect an s-wave ground state for a particle in a spherically symmetric potential.Thefore expectation value of the energy in our trial wave function is given by the integral

$$E = 4\pi C^2 \int dr\, r^2 \left[\frac{\hbar^2}{2m} \lambda^2 e^{-2\lambda r} - \alpha e^{-2(\mu+\lambda)r} \right],$$

which we can rewrite as

$$E = 4\pi C^2 \int dx\, x^2 e^{-x} \left(\frac{\hbar^2 \lambda^2}{2m} \left(\frac{1}{2\lambda} \right)^3 - \frac{\alpha}{8(\mu+\lambda)^3} \right),$$

or, using part (a),

$$E = \frac{\hbar^2 \lambda^2}{2m} - \alpha \left(\frac{\lambda}{\mu+\lambda} \right)^3.$$

(c) **(3 points)** We minimize E with respect to λ:

$$\frac{\partial E}{\partial \lambda} = \frac{\hbar^2 \lambda}{m} - 3\alpha \left(\frac{\lambda}{\mu+\lambda} \right)^2 \frac{\mu}{(\mu+\lambda)^2} = 0.$$

This has the obvious solution $\lambda = 0$; the other solutions are found by solving the quartic equation $(\mu+\lambda)^4 - 3\alpha m \lambda \mu/\hbar^2 = 0$. By glancing at the quartic formula, it is easy to see that the quartic equation has no real roots unless $81\alpha m - 256\mu^2\hbar^2 > 0$, or, in other words, only for $\alpha > \frac{256\mu^2\hbar^2}{81m}$ does E have extrema other than at $\lambda = 0$. Therefore for small α, minimum value of $E(\lambda)$ is 0, i.e. there are no bound states. [Note: You can solve the quartic equation $(\mu+\lambda)^4 = a\lambda$ using Mathematica, and you can see the occurence of $\sqrt{27a^4 - 256a^3\mu^3}$ at several places. In order to have one or more real solutions, you need $27a - 256\mu^3$ to be poitive. This is where you get the above condition.]

When $\lambda = 0$, the energy also vanishes, and we are left with something that looks very much like a zero momentum plane wave. The wave function is distributed uniformly through space.

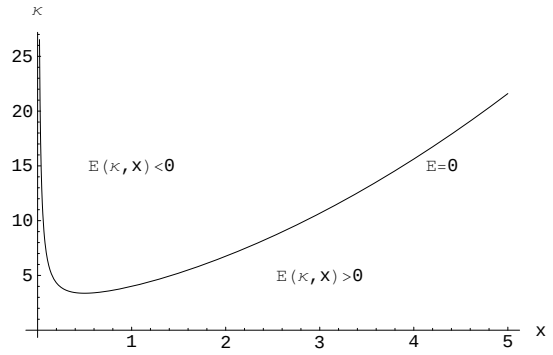

Figure 1: $\kappa = \frac{(1+x)^3}{2x}$

(Of course, this means that the probability of finding the particle at any specific point goes to zero as the volume of space goes to infinity.)

(d) **(3 points)** In terms of our dimensionless variables x and κ, we find

$$\begin{aligned} \mathcal{E} &= \frac{1}{2}\left(\frac{\lambda}{\mu}\right)^2 - \frac{m\alpha}{\hbar^2\mu^2}\left(\frac{\lambda/\mu}{1+\lambda/\mu}\right)^3 \\ &= \frac{1}{2}x^2 - \kappa\left(\frac{x}{1+x}\right)^3 . \end{aligned}$$

We would like to know when it is possible to have $\mathcal{E} = 0$, as this is the dividing line between having a bound state and having no bound states. We plot this dividing line as a function of x and κ in figure 1. To have $\mathcal{E} = 0$, we must have $\kappa = \frac{(1+x)^3}{2x}$. The minimum value of κ satisfying that condition is obtained by setting $\frac{\partial\kappa}{\partial x} = 0$, yielding

$$\kappa_{min} = 3.375, \qquad\qquad x = \frac{1}{2}.$$

(e) **(3 points)** Recall that the variational method gives only an upper bound on the ground state energy. If $\mathcal{E} < 0$, we know that there exists a bound state, but if $\mathcal{E} > 0$, we cannot conclude that there is no bound state. Therefore, the previous section gives us neither a minimum nor a maximum value of α required for a bound state. All it tells us is that if $\alpha \geq \frac{\hbar^2\mu^2\kappa_{min}}{m}$, then we know that a bound state exists, while if $\alpha < \frac{\hbar^2\mu^2\kappa_{min}}{m}$, we do not know if a bound state exists.

2. **Several proofs constructed via the variational method (10 points)**

(a) **6 points** Suppose the wave function has a zero of degree p at $x = x_0$, that is in the vicinity of x_0, it takes on the form $a(x - x_0)^p$ for some a. There will in general be terms in $(x - x_0)$ of higher-than-p-order, but we will work in a limit in which only that part of the wave function arbitrarily close to x_0 matters, and so these higher order terms can be neglected. Following the hint, in the vicinity of x_0 our initial trial wave function takes the form

$$\psi(x) = a|x - x_0|^p \ .$$

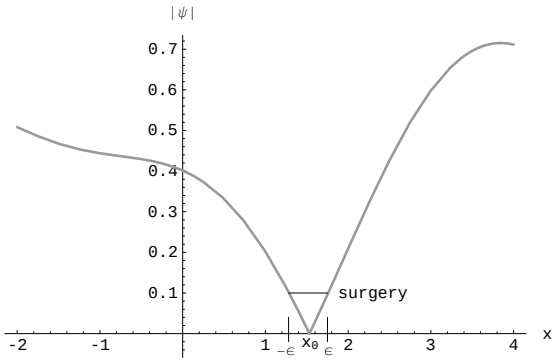

Figure 2: Trial wave functions. The gray line is $|\psi|$; the horizontal black line is slight modification made locally around $x = x_0$.

Note that the integrand in the energy integral,

$$\int \left(\frac{\hbar^2}{2m} |\nabla\psi|^2 + V |\psi|^2 \right) dx$$

has two terms, one proportional to $V|\psi|^2$ and one proportional to $|\nabla\psi|^2$, and therefore taking the absolute value has not changed the energy of our initial trial wave function. We now show that the energy of this trial wave function can be lowered by "chopping off its tip." That is, we leave the wave function as it is for $|x - x_0| > \epsilon$, and for $|x - x_0| < \epsilon$ we replace it by $\psi = a\epsilon^p$, in otherwords a horizontal line segment extending from $x - x_0 = -\epsilon$ to $x - x_0 = +\epsilon$, with ψ a constant given by $a\epsilon^p$. See figure 2. This surgery modifies the potential energy by an amount of order

$$2V(x_0) \int_0^\epsilon a^2 \left(\epsilon^{2p} - y^{2p} \right) dy = 2V(x_0) a^2 \epsilon^{2p+1} \left(1 - \frac{1}{2p+1} \right)$$

where we have defined $y = x - x_0$, which is of order ϵ^{2p+1}. This modification could be positive or negative. This surgery *reduces* the kinetic energy by an amount of order

$$2\frac{\hbar^2}{2m} \int_0^\epsilon a^2 y^{2(p-1)} dy = \frac{\hbar^2}{m(2p-1)} a^2 \epsilon^{2p-1}.$$

It is a reduction in kinetic energy because the surgery has introduce a region with $\nabla\psi = 0$, hence zero kinetic energy, in place of a region where the kinetic energy was positive. For sufficiently small ϵ, the reduction in kinetic energy (of order ϵ^{2p-1}) is greater than the change in potential energy (of order ϵ^{2p+1}), and the total energy is thus reduced. Since the surgery has removed the zero, we conclude that the energy of any trial wave function with a zero can always be lowered by doing this kind of surgery that removes the zero. Therefore we conclude that the ground state wave function has no nodes.

(b) **(1 point)** Let ϕ_1 and ϕ_2 be degenerate ground states. Then both ϕ_1 and ϕ_2 are nodeless, by part (a), and therefore can never change sign. Therefore $\int dx\, \phi_1(x)\phi_2(x)$ is always strictly positive or strictly negative, and cannot vanish. This is a contradiction, since ϕ_1 and ϕ_2 are supposed to be independent energy eigenstates, and therefore orthogonal.

(c) **(3 points)**For Simplicity let us translate our co-ordinate system such that $x \to x + x_0$. Now we can use the trial wavefunction $\psi = Nexp(-\lambda|x|)$. We can easily calculate $N = \sqrt{\lambda}$. The kinetic energy is therefore

$$\begin{aligned} T &= \frac{\hbar^2}{2m}\int dx \left|\frac{d\psi}{dx}\right|^2 \\ &= \frac{\hbar^2\lambda^2}{2m}. \end{aligned}$$

Taylor expanding potential energy about $\lambda = 0$ we get,

$$\int dx|\psi|^2 V(x) = \lambda \int dx V(x) + \mathcal{O}(\lambda^2).$$

But $\int dx V(x) < 0$, as potential is negative between x_1 and x_2 and 0 every where else. Now as $\lambda \to 0$, the kinetic energy goes to 0 as λ^2, but the contribution from the potential energy, goes to 0 only as λ with a negative coefficient. Therefore there exists a λ small enough such that total energy is less than 0. Hence, the ground state has negative energy, and is a bound state.

3. **The hydrogen molecular ion (20 points)**

(a) **(3 points)** Normalizing the trial wave function $\psi = A(\psi_g(r_1) + \psi_g(r_2))$ gives

$$1 = 2A^2\left(1 + \int r^2 dr d\Omega \psi_g(r_1)\psi_g(r_2)\right).$$

In order to go further, we need to specify some coordinates. We will follow Griffiths, and put the first proton at the origin, so that $r = r_1$, while the second proton lives on the z axis, so that $r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$. We therefore need to evaluate the integral

$$\int r^2 dr\, d\Omega \psi_g(r_1)\psi_g(r_2) = \frac{1}{\pi a_0^3}\int d\phi \sin\theta d\theta r^2 dr\, e^{-(r+\sqrt{r^2+R^2-2rR\cos\theta})/a_0}.$$

We do the angular integrals using Griffiths' trick for the θ integral, to get

$$-\frac{2}{a_0^2 R}\int r dr\, e^{-r/a_0}\left(e^{-(r+R)/a_0}(r+R+a_0) - e^{-|r-R|/a_0}(|r-R|+a_0)\right).$$

The integrals above can be done by parts, so that we find

$$\int r^2 dr\, d\Omega \psi_g(r_1)\psi_g(r_2) = e^{-R/a_0}\left[1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right].$$

We therefore find

$$A^2 = \frac{1}{2}\left(1 + e^{-R/a_0}\left[1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right]\right)^{-1}. \tag{1}$$

(b) **(7 points)** We start with Griffiths' expression,

$$\begin{aligned} \langle H\rangle &= E_1 - 2A^2e^2\left(\langle\psi_g(r_1)|\frac{1}{r_2}|\psi_g(r_1)\rangle + \langle\psi_g(r_1)|\frac{1}{r_1}|\psi_g(r_2)\rangle\right) \\ &\equiv E_1 - \frac{2A^2e^2}{a_0}(D+X). \end{aligned}$$

We start with the direct term D. It is actually simpler to compute

$$\frac{D}{a_0} = \langle\psi_g(r_2)|\frac{1}{r_1}|\psi_g(r_2)\rangle = \frac{1}{\pi a_0^3}\int d\Omega r dr\, e^{-2\sqrt{r^2+R^2-2rR\cos\theta}/a_0}.$$

We can perform the θ integral using the same trick as in part (a),

$$\begin{aligned}\int \sin\theta d\theta e^{-2\sqrt{r^2+R^2-2rR\cos\theta}/a_0} &= \frac{1}{rR}\int_{|r-R|}^{R+r} y dy e^{-2y/a_0} \\ &= -\frac{a_0}{2rR}\left(e^{-2(r+R)/a_0}(R+r+\frac{a_0}{2}) - e^{-2|r-R|/a_0}(|r-R|+\frac{a_0}{2})\right).\end{aligned}$$

We are now left with some easy (if irritating) integrals over r:

$$\begin{aligned}\frac{D}{a_0} &= -\frac{1}{Ra_0^2}\int dr\left(e^{-2(r+R)/a_0}(R+r+\frac{a_0}{2}) - e^{-2|r-R|/a_0}(|r-R|+\frac{a_0}{2})\right) \\ &= \frac{1}{R} - \frac{1}{a_0}\left(1+\frac{a_0}{R}\right)e^{-2R/a_0}.\end{aligned}$$

The evaluation of the exchange term X is similar:

$$\frac{X}{a_0} = \langle\psi_g(r_1)|\frac{1}{r_1}|\psi_g(r_2)\rangle = \frac{1}{\pi a_0^3}\int d\Omega r dr\, e^{-(r+\sqrt{r^2+R^2-2rR\cos\theta})/a_0}.$$

The same trick can be used to perform the θ integral, leaving

$$\frac{X}{a_0} = -\frac{2}{a_0^2 R}\int dr e^{-r/a_0}\left[e^{-(r+R)/a_0}(r+R+a_0) - e^{-|r-R|/a_0}(|r-R|+a_0)\right].$$

Performing the r integrals, we find finally

$$X = \left(1+\frac{R}{a_0}\right)e^{-R/a_0}.$$

Thus, the expectation value of the Hamiltonian in the trial state is

$$\langle H\rangle = E_1 - \frac{2A^2e^2}{a_0}\left[\left(1+\frac{R}{a_0}\right)e^{-R/a_0} + \frac{a_0}{R} - \left(1+\frac{a_0}{R}\right)e^{-2R/a_0}\right].$$

Defining $w = R/a_0$ and using equation (1) for A^2, we find

$$\langle H\rangle = E_1 + 2\frac{E_1}{w}\frac{(w+w^2)e^{-w} + 1 - (w+1)e^{-2w}}{1+(1+w+\frac{1}{3}w^2)e^{-w}},$$

where I have used $E_1 = -\frac{e^2}{2a_0}$.

To find the total energy of the system, we need to add the proton-proton electromagnetic repulsion, $V_{pp} = -2\frac{a_0}{R}E_1 = -\frac{2}{w}E_1$. This yields

$$\begin{aligned}E_{total} &= E_1\left[1+\frac{2}{w}\frac{(\frac{2}{3}w^2-1)e^{-w} - (w+1)e^{-2w}}{1+(1+w+\frac{1}{3}w^2)e^{-w}}\right] \\ &= -E_1\left[-1+\frac{2}{w}\frac{(1-\frac{2}{3}w^2)e^{-w} + (w+1)e^{-2w}}{1+(1+w+\frac{1}{3}w^2)e^{-w}}\right] \\ &= -E_1 F(w).\end{aligned}$$

(c) **(2 points)** Numerically, we can find the minimum of $F(w)$:

$$w_0 = 2.49283 \qquad\qquad F(w_0) = -1.12966.$$

(I used FindMinimum in Mathematica.) We can use this to estimate the equilibrium separation,

$$R_0 = a_0 w_0 = 1.32 \times 10^{-8} \text{ cm},$$

and an upper bound on the energy of the system,

$$E_{ground} < -E_1 F(w_0) = -15.36 \text{ eV}.$$

This energy is *less* than -13.6 eV, so the system binds.

(d) **(5 points)** Using Mathematica, I find $F''(w_0) = 0.1257$. Now,

$$\frac{\partial^2 \langle H \rangle}{\partial R^2} = -E_1 \frac{\partial}{\partial R}\left(\frac{\partial F}{\partial w}\frac{1}{a_0}\right) = -\frac{E_1}{a_0^2}F''(w_0).$$

Semi-classically, the average kinetic energy is zero in equilibrium, so we can conclude $\frac{\partial^2 \langle V \rangle}{\partial R^2} = -\frac{E_1}{a_0^2}F''(w_0)$.

We now want to think about the hydrogen nuclei as oscillating about their center of mass. This problem separates into the free motion of the center of mass, described as a particle of mass $M_T = M_1 + M_2 = 2m_p$, and the relative motion, described as a particle of reduced mass $\mu = \frac{M_1 M_2}{M_1 + M_2} = m_p/2$. Therefore, the oscillation frequency is found through $\frac{1}{2}m_p\omega^2 = -\frac{E_1}{a_0^2}F''(w_0)$, or

$$\begin{aligned} \omega^2 &= -\frac{2E_1}{m_p a_0^2}F''(w_0) \\ &= 0.0506\left(\frac{\text{eV}}{\hbar}\right)^2, \end{aligned}$$

so that

$$\hbar\omega = 0.2251 \text{ eV}.$$

We want to estimate how many bound vibrational levels we can excite before the energy of vibration is sufficient to disassociate the hydrogen molecule. Our ground state is, from our variational calculation, at the energy $E_{ground} = E_1 - 1.76$ eV. The energy of the nth excited level will be $E_n = E_1 - 1.76 \text{ eV} + n\hbar\omega$. The maximum allowed n is given by

$$n_{max} = \frac{1.76 \text{ eV}}{\hbar\omega} = 7.8,$$

but since n must be an integer, we find that there are 8 energy levels, for $n = 0, 1, \ldots, 7$.

(e) **(3 points)** We now set $\psi = A(\psi_g(r_1) - \psi_g(r_2))$. This gives us

$$A^2 = \frac{1}{2}\left[1 - e^{-R/a_0}\left(1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right)\right]^{-1},$$

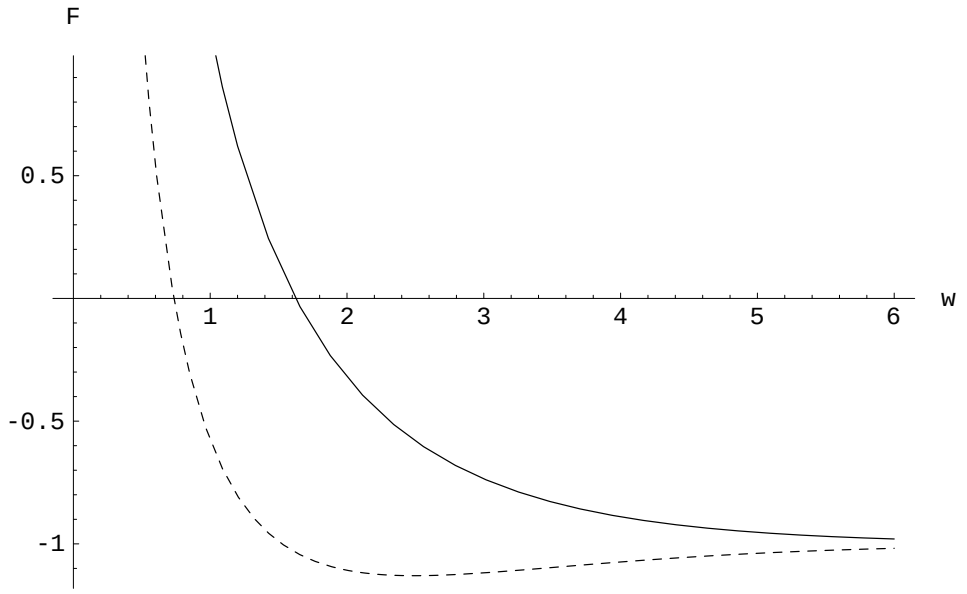

Figure 3: $F_2(w)$. Also shown is $F(w)$, with a dashed line.

while the expectation value of the energy becomes

$$\langle H\rangle = E_1 - \frac{2A^2e^2}{a_0}(D-X).$$

Propagating these two sign changes gives us

$$\langle H\rangle = -E_1(-1+\frac{2}{w}\frac{(1+w)e^{-2w}-(1-\frac{2}{3}w^2)e^{-w}}{1-e^{-w}(1+w+\frac{1}{3}w^2)} \equiv -E_1F_2(x).$$

We plot $F_2(w)$ and $F(w)$ in figure 3, and note that F_2 has no local minimum.

4. **Tunneling and the Stark effect (18 points)**

(a) **(2 points)** For an infinitely deep square well of width d, the energy of the ground state is $E_{\infty,0} = \frac{\hbar^2\pi^2}{2md^2}$ (this is the amount by which ground state energy is above the bottom of the potential well). Since the zero of energy is at the top of the well rather than the bottom in this problem, we estimate $E_0 = \frac{\hbar^2\pi^2}{2md^2} - V_0$. Full credit will be given on writing only $E_{\infty,0}$.

Optional part: To show that true ground state is lower than this, use variational principle. Consider potential $V(x) = 0$ for $|x| < d/2$ but $V(x) = V_0$ for $|x| > d/2$. Take the trial wavefunctions to be $\psi(x) = \sqrt{2/d}\cos(\pi x/d)$ for $|x| < d/2$ and 0 everywhere else. Of course this is the exact ground state wavefunction for the infinite well potential and indeed $\langle\psi|H|\psi\rangle = E_{\infty,0}$, where H is hamiltonian corresponding to the potential mentioned above, which is nothing but the square well potential of this problem shifted by V_0. Therefore the true ground state must be lower than $E_{\infty,0}$.

(b) **(2 points)** A sketch of the potential is in figure 4.

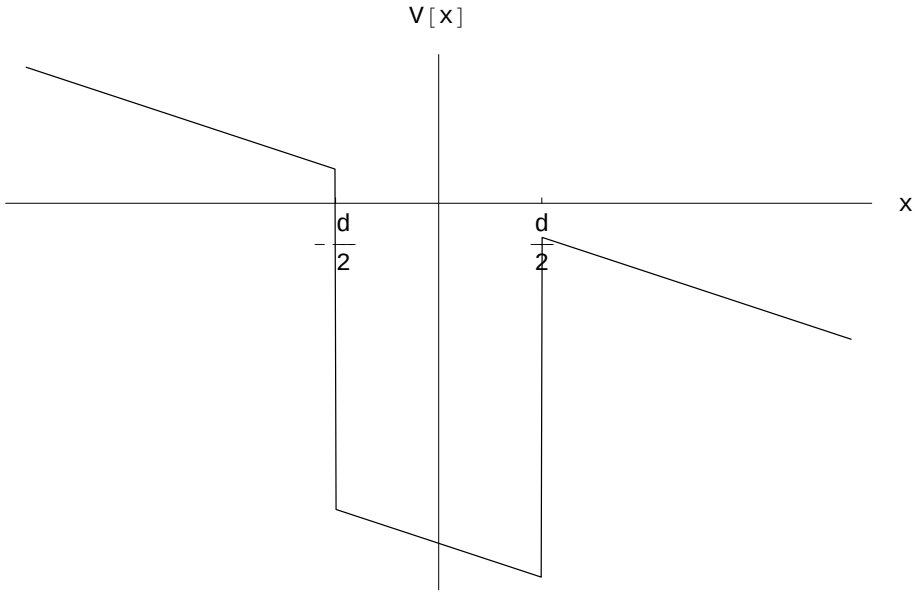

Figure 4: A square well potential in a constant electric field.

The potential no longer binds states because it is unbounded from below; a particle trapped in the well can reduce its energy by tunneling out to $x = \infty$.

(c) **(5 points)** To use semiclassical approximation to find the tunneling probability, we first need to find the classical turning point. This occurs at

$$x_t = -\frac{E_0}{e\mathcal{E}} = \frac{V_0 - \frac{\hbar^2\pi^2}{2md^2}}{e\mathcal{E}}.$$

The tunneling probability is given semi-classically by

$$T \simeq e^{-\frac{2}{\hbar}\int_{d/2}^{x_t} dx\, |p(x)|}.$$

The integral appearing in the exponential is

$$\begin{aligned}\int_{d/2}^{x_t} dx\, \sqrt{2m(V - E_0)} &= \sqrt{2me\mathcal{E}} \int_{d/2}^{x_t} dx\, \sqrt{x_t - x} \\ &= \frac{2}{3}\sqrt{2me\mathcal{E}} \left(x_t - \frac{d}{2}\right)^{3/2}.\end{aligned}$$

Since $e\mathcal{E}d \ll V_0$, the barrier is very wide, and we do indeed have $x_t \gg d$:

$$\frac{x_t}{d} = \frac{V_0 - \frac{\hbar^2\pi^2}{2md^2}}{e\mathcal{E}d} \simeq \frac{V_0}{e\mathcal{E}d} \gg 1,$$

and therefore

$$T \simeq e^{-\frac{4}{3\hbar}\frac{\sqrt{2mV_0^3}}{e\mathcal{E}}}. \tag{2}$$

(d) **(5 points)** Classically, the time associated with this particle is $t_0 = \frac{2d}{v}$, the time it takes to bounce back and forth once. Here the velocity is $v = \sqrt{\frac{2E_{\infty,0}}{m}} = \frac{\hbar\pi}{md}$. So, if we have N particles in the box, all N hit the right wall in time t_0, therefore in time dt, Ndt/t_0 particles hit the right wall and escape with the probablity T. Hence, differential rate of loss of particle number is given by:

$$dN = -TN\frac{dt}{t_0},$$

and therefore

$$N = N_0 e^{-Tt/t_0},$$

where N_0 is the initial number of particles. The lifetime of the bound state is thus,

$$\tau = \frac{t_0}{T} = \frac{2md^2}{T\pi\hbar}.$$

(e) **(2 points)** Plugging in the given numbers, $T = e^{-86115}$. This gives the lifetime of $\tau = 4 \times 10^{37383}$ s —which is unbelievably long! The age of the universe is 13.7 billion years, which is 4.3×10^{17} s.

(f) **(2 points)** Since we found that $T = \exp(-\text{const.}/\mathcal{E})$, and $\tau \propto \frac{1}{T}$, we have already demonstrated that the lifetime goes like $\exp(1/\mathcal{E})$. If we Taylor expand $e^{1/\mathcal{E}}$ about $\mathcal{E} = 0$, we get zero to any finite order in $\mathcal{E}$, and hence you cannot see tunnelling at any order in perturbation theory.