

Physics 125c
Course Notes
Approximate Methods
Solutions to Problems
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1 Exercises

1. Prove the theorem quoted in section ??:

Theorem: If we have a normalized function $|\psi\rangle$ such that

$$E_0 \leq \langle \psi | H | \psi \rangle \leq E_1, \quad (1)$$

then

$$E_0 \geq \langle \psi | H | \psi \rangle - \frac{\langle H \psi | H \psi \rangle - \langle \psi | H | \psi \rangle^2}{E_1 - \langle \psi | H | \psi \rangle}. \quad (2)$$

Solution: The theorem is equivalent to the statement

$$\langle \psi | H^2 \psi \rangle - \langle \psi | H | \psi \rangle^2 \geq (\langle \psi | H | \psi \rangle - E_0)(E_1 - \langle \psi | H | \psi \rangle). \quad (3)$$

Notice that if we add a constant A to H , obtaining $H' = H + A$ (hence also $E_n \rightarrow E'_n = E_n + A$), both sides of this inequality are unaltered. The left hand side is a measure of the width of the energy distribution and is not altered by shifting the energy scale. Likewise, the right hand side only depends on energy differences. Thus, as long as the spectrum of H is bounded below, the problem is equivalent to a problem where the spectrum is non-negative. In particular, we may simplify by taking $E_0 = 0$.

Hence, consider:

$$\begin{aligned} \langle \psi | H^2 \psi \rangle - \langle \psi | H | \psi \rangle^2 - \langle \psi | H | \psi \rangle(E_1 - \langle \psi | H | \psi \rangle) \\ = \langle \psi | H^2 \psi \rangle - E_1 \langle \psi | H | \psi \rangle \end{aligned} \quad (4)$$

$$= \sum_{n=0} |c_n|^2 E_n^2 - E_1 \sum_{n=0} |c_n|^2 E_n \quad (5)$$

$$= \sum_{n=0} |c_n|^2 E_n (E_n - E_1) \quad (6)$$

$$= \sum_{n=1} |c_n|^2 E_n (E_n - E_1), \quad \text{since } E_0 = 0, \quad (7)$$

$$\geq 0, \quad \text{since each term in the sum is non-negative.}$$

2. Let us pursue our variational approach to the estimation of ground state energy levels of atoms to the “general” case. We consider an atom with nuclear charge Z , and N electrons. The Hamiltonian of interest is:

$$H(Z, N) = H_{\text{kin}} - ZV_c + V_e \quad (8)$$

$$H_{\text{kin}} = \sum_{n=1}^N \frac{\mathbf{p}_n^2}{2m}, \quad (9)$$

where (10)

$$V_c = \alpha \sum_{n=1}^N \frac{1}{|\mathbf{x}_n|} \quad (11)$$

$$V_e = \alpha \sum_{N \geq j > k \geq 1} \frac{1}{|\mathbf{x}_k - \mathbf{x}_j|} \quad (12)$$

$$m = \text{electron mass} \quad (13)$$

$$\alpha = \text{fine structure constant.} \quad (14)$$

Denote the ground state energy of $H(Z, N)$ by $-B(Z, N)$, with $B(Z, 0) = 0$.

- (a) Generalize the variational calculation we performed for the ground state of helium to the general Hamiltonian $H(Z, N)$. Thus, select your “trial function” to be a product of N identical “hydrogen atom ground state” functions. Determine the resulting lower bound $\hat{B}(Z, N)$ on $B(Z, N)$ (*i.e.*, an upper limit on the ground state energies).

Solution: Let Ze be the fixed nuclear charge in the Hamiltonian, and let z be the effective Z variational parameter. The trial wave function we are told to use is thus:

$$\psi_{ZN}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \prod_{n=1}^N \sqrt{\frac{z^3}{\pi a_0^3}} e^{-\frac{z}{a_0}(r_n)}, \quad a_0 = \frac{1}{m\alpha}. \quad (15)$$

The expectation value of the total kinetic energy for this trial function is:

$$H_{\text{kin}} = N \langle \psi | \frac{p_1^2}{2m} | \psi \rangle = Nz^2 \frac{1}{2} m\alpha^2. \quad (16)$$

The expectation value of the potential energy of the electrons in the nuclear electric field is:

$$-ZV_c = -NZzm\alpha^2. \quad (17)$$

The expectation value of the potential energy of the electrons in the fields of the other electrons is:

$$V_e = \frac{N(N-1)}{2} z \frac{1}{2} \frac{5}{4} m\alpha^2. \quad (18)$$

Putting these terms together, we have

$$\langle H(Z, N) \rangle_z = \frac{1}{2} m\alpha^2 N z \left[z - 2Z + \frac{5}{8}(N-1) \right] \quad (19)$$

We minimize with respect to z :

$$0 = \frac{d}{dz} \left[z^2 - 2Zz + \frac{5}{8}(N-1)z \right] = 2z - 2Z + \frac{5}{8}(N-1). \quad (20)$$

Thus, the minimum occurs at

$$z = Z - \frac{5}{16}(N-1) \quad (21)$$

The variational bound on the (negative of the) ground state energies is then:

$$\hat{B}(Z, N) = -\langle H(Z, N) \rangle_{\min} = \frac{1}{2} m\alpha^2 N \left[Z - \frac{5}{16}(N-1) \right]^2. \quad (22)$$

- (b) Make a simple table comparing your variational bounds with the observed ground state energies for lithium, beryllium, and nitrogen. Note that a simple web search for “ionization potentials” will get you a multitude of tables of observed values, or you can look at a reference such as the CRC Press’s *Handbook of Chemistry and Physics*. The table entries are typically of the form:

$$B(Z, N) - B(Z, N-1).$$

Solution: A Google search on “ionization potentials” results in many suitable hits, including:

http://www.chemistrycoach.com/ionization_potentials_f.htm

The ionization potentials for lithium, beryllium, and nitrogen are reproduced in Table 2b.

The predicted bounds on the energies, according to Eqn. 22, are compared with the observed values in Table 2b.

Ionization Potentials for Lithium, Beryllium, and Nitrogen
 (from http://www.chemistrycoach.com/ionization_potentials.f.htm)

	Lithium	Beryllium	Nitrogen
1st I.P.	5.4	9.3	14.5
2nd I.P.	75.6	18.2	29.6
3rd I.P.	122	154	47.5
4th I.P.		218	77.5
5th I.P.			97.9
6th I.P.			552
7th I.P.			667

Comparison of Variational Prediction with Measured Energies

N	Lithium		Beryllium		Nitrogen	
	Pred.	Meas.	Pred.	Meas.	Pred.	Meas.
1	122.5	122	217.7	218	666.7	667
2	196.5	198	370.0	372	1217.0	1219
3	230.2	203	464.9	390	1658.8	1317
4			510.4	400	2000.2	1394
5					2249.2	1442
6					2413.6	1472
7					2501.5	1486

- (c) Do your results make sense? If not, can you figure out what is wrong, and whether the calculation we did for He is to be trusted?

Solution: Note that for $N = 1$, the calculation is “exact”, up to the approximations made and effects neglected. The differences between predicted and observed values for $N = 1$ are an indication of the uncertainty due to the neglect in these matters, and possibly experimental uncertainties.

We see that for $N > 2$, the computed bounds are always violated by the data. The trial wave function for $N > 2$ is not properly antisymmetric under interchange of the electrons, hence is not in the Hilbert space. The calculation for He is still all right, since the electron has a spin degree of freedom – A symmetric spatial wave function for two electrons is permitted, as the spin wave function can be antisymmetric.

The computation for $N = 2$ should be all right, and we see that the bound is always on the side it is supposed to be. Indeed, we do rather well, always getting within a percent of the actual energy.

3. We consider the quantum mechanics of a particle in the earth’s gravitational field:

$$V(r) = -G \frac{Mm}{r} \quad (23)$$

$$= -G \frac{Mm}{R+z} \quad (24)$$

$$\approx -G \frac{Mm}{R} + mgz \quad (25)$$

where (26)

$$M = \text{mass of earth} \quad (27)$$

$$m = \text{mass of particle} \quad (28)$$

$$r = \text{distance from center of earth} \quad (29)$$

$$G = \text{Newton’s gravitational constant} \quad (30)$$

$$R = \text{radius of earth} \quad (31)$$

$$z = \text{height of particle above surface of earth} \quad (32)$$

$$g = GM/R^2. \quad (33)$$

We may drop the constant term in our discussion, and consider only the mgz piece, with $z \ll R$. We further assume that no angular momen-

tum is involved, and treat this as a one dimensional problem. Finally, assume that the particle is unable to penetrate the earth's surface.

- (a) Make a WKB calculation for the energy spectrum of the particle.

Solution: The potential is

$$V(z) = mgz. \quad (34)$$

We need the turning points z_1 and z_2 :

$$V(z_1) = V(z_2) = E \quad (35)$$

In this case, since we hit the ground at $z = 0$, and can go no further, $z_1 = 0$. The other turning point is at

$$z_2 = \frac{E}{mg}. \quad (36)$$

Now we compute the function:

$$f(E_n) = \int_{z_1(E_n)}^{z_2(E_n)} \sqrt{2m[E_n - V(z)]} dz \quad (37)$$

$$= \int_0^{E_n/mg} \sqrt{2m(E_n - mgz)} dz \quad (38)$$

$$= \left(n + \frac{1}{2}\right) \pi. \quad (39)$$

That is,

$$\left(n + \frac{1}{2}\right) \pi = \sqrt{2mE_n} \frac{E_n}{mg} \int_0^1 \sqrt{y} dy \quad (40)$$

$$= \frac{2}{3g} \sqrt{\frac{2}{m}} E_n^{3/2}. \quad (41)$$

Solving for E_n , we obtain the estimated bound state energy spectrum:

$$E_n = \left(\frac{9\pi^2}{8} mg^2\right)^{\frac{1}{3}} \left(n + \frac{1}{2}\right)^{\frac{2}{3}}. \quad (42)$$

- (b) If the particle is an atom of atomic weight $A \sim 100$, use the result of part (a) to estimate the particle's ground state energy (in eV). Is sunlight likely to move the particle into excited states?

Solution: If $A = 100$, then $m \sim 100 \times 10^9$ eV. Also,

$$g \sim 10\text{m/s}^2 \quad (43)$$

$$\begin{aligned} &\sim 10\text{m/s}^2 \times \frac{1}{(3 \times 10^8\text{m/s})^2} \times 200\text{MeV}\cdot\text{fm} \times 10^{-15}\text{m}/\text{fm} \\ &\sim 2 \times 10^{-23} \text{ eV}. \end{aligned} \quad (44)$$

The ground state energy is ($n = 0$):

$$E_0 = \left(\frac{9\pi^2}{8} mg^2 \right)^{\frac{1}{3}} \left(\frac{1}{2} \right)^{\frac{2}{3}} \quad (45)$$

$$\sim 10^{-12} \text{ eV}. \quad (46)$$

Since photons in sunlight have energies of order eV, they will readily excite such atoms into highly excited states in the gravitational potential.

- (c) Now make a variational calculation for the ground state energy (*i.e.*, an upper bound thereon). Pick a “sensible” trial wave function, at least in the sense that it satisfies the right boundary conditions. Compare your result with the ground state level from the WKB approximation.

Solution: The wave function must vanish at $z = 0$ and at $z = \infty$. A simple trial function which satisfies these boundary conditions is:

$$\psi(z) = \frac{z}{\sqrt{2R^3}} e^{-z/2R}, \quad (47)$$

where the variational parameter is R .

We must evaluate the expectation value of the Hamiltonian for our trial wave function. The kinetic energy part is:

$$\langle T \rangle = \int_0^\infty \frac{z}{\sqrt{2R^3}} e^{-z/2R} \left(-\frac{1}{2m} \frac{d^2}{dz^2} \right) \frac{z}{\sqrt{2R^3}} e^{-z/2R} dz \quad (48)$$

$$= \frac{1}{4mR^3} \int_0^\infty \frac{1}{R} \left(z - \frac{z^2}{4R} \right) e^{-z/R} dz \quad (49)$$

$$= \frac{1}{8mR^2}. \quad (50)$$

The potential energy part is:

$$\langle V \rangle = \int_0^\infty \frac{z}{\sqrt{2R^3}} e^{-z/2R} mgz \frac{z}{\sqrt{2R^3}} e^{-z/2R} dz \quad (51)$$

$$= 3mgR. \quad (52)$$

Thus, we wish to minimize the quantity $3mgR + \frac{1}{8mR^2}$ as a function of R . The minimum occurs at

$$R = \left(\frac{1}{12m^2g} \right)^{\frac{1}{3}}. \quad (53)$$

Thus, the variational bound on the ground state energy is

$$E_0 \leq \left[\left(\frac{3}{2} \right)^5 mg^2 \right]^{1/3}. \quad (54)$$

We note that this bound is slightly larger than the WKB estimate:

$$\left[\left(\frac{3}{2} \right)^5 mg^2 \right]^{1/3} / \left(\frac{9\pi^2}{32} mg^2 \right)^{1/3} = \left(\frac{27}{\pi^2} \right)^{1/3}. \quad (55)$$

4. We discussed the method of stationary phase in section ???. Recall that the problem it addresses is to evaluate integrals of the form:

$$I(\epsilon) = \int_{-\infty}^{\infty} f(x) e^{i\theta(x)/\epsilon} dx, \quad (56)$$

where f and θ are real, and $\epsilon > 0$. We showed that, in the situation where ϵ is very small, and θ has a stationary point at $x = x_0$, this integral is approximately:

$$I(\epsilon) = \sqrt{\epsilon} f(x_0) e^{i\theta(x_0)/\epsilon} e^{i\frac{\pi}{4} \text{sign}[\theta''(x_0)]} \sqrt{\frac{2\pi}{|\theta''(x_0)|}} [1 + O(\epsilon)]. \quad (57)$$

If there is more than one stationary point, then the contributions are to be summed.

To get a little practice applying this method, evaluate the following integral for large t :

$$J(t) = \int_0^1 \cos [t(x^3 - x)] dx. \quad (58)$$

Solution: To start to get it into the desired form, write

$$J(t) = \Re \int_0^1 e^{i(t(x^3-x))} dx. \quad (59)$$

Thus, $f(x) = 1$, $\theta(x) = x^3 - x$, and $\epsilon = 1/t$. The first two derivatives are $\theta'(x) = 3x^2 - 1$ and $\theta''(x) = 6x$. The first derivative is zero at $x = \pm 1/\sqrt{3}$. The zero at $x_0 = 1/\sqrt{3}$ falls within the range of the integral, so this is the only stationary point of interest. The value of θ at the stationary point is $\theta(x_0) = -2/3\sqrt{3}$. The second derivative at the stationary point is $\theta''(x_0) = 2\sqrt{3}$.

Plugging into our stationary phase formula, we get:

$$J(t) \approx \Re \frac{1}{\sqrt{t}} e^{-\frac{2it}{3\sqrt{3}}} e^{i\pi/4} \sqrt{\frac{2\pi}{2\sqrt{3}}} \quad (60)$$

$$= \Re \sqrt{\frac{\pi}{t\sqrt{3}}} e^{i\left(\frac{\pi}{4} - \frac{2t}{3\sqrt{3}}\right)} \quad (61)$$

$$= \sqrt{\frac{\pi}{t\sqrt{3}}} \cos\left(\frac{\pi}{4} - \frac{2t}{3\sqrt{3}}\right). \quad (62)$$

5. I suggested in section ?? that you consider the classical correspondence for the time delay (or advance) of the asymptotic motion due to scattering on a potential. Let us pursue this here. Consider one-dimensional motion. A particle of mass m is incident from the left on a potential:

$$V(x) = \begin{cases} -K & x \in (-\Delta/2, \Delta/2) \\ 0 & \text{otherwise.} \end{cases} \quad (63)$$

We wish to solve for the motion for large x at large times.

- (a) Let's do the quantum mechanics calculation first. Suppose that our momentum space wave function at early time is a gaussian wave packet:

$$\hat{\psi}(p) = \left[\frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{1}{2}\left(\frac{p-q}{\sigma}\right)^2} \right]^{1/2}. \quad (64)$$

What is $\psi(x, t)$ for large times and large x ? Describe the motion, relative to what it would be if $K = 0$.

(b) Now do the same problem classically. That is, solve for the motion at large times and large x . Again, compare the result with what it would be for $K = 0$. Contrast with the quantum result.

6. We have solved the Schrödinger equation for the Hydrogen atom with Hamiltonian:

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}.$$

The kinetic energy term is non-relativistic – the actual kinetic energy will have relativistic corrections.

(a) Obtain an expression for the next order relativistic (kinetic energy) correction to the energy spectrum of hydrogen. It is convenient to avoid taking multiple derivatives by using the unperturbed Schrödinger equation to eliminate them. Thus, write your expression in terms of the unperturbed energies and expectation values of $\frac{e^2}{r}$ and $(\frac{e^2}{r})^2$. Do not actually do the integration over r here, but reduce the problem to such integrals. Make sure you understand all of your steps.

Solution: The relativistic kinetic energy is

$$T = \sqrt{p^2 + m^2} - m \tag{65}$$

$$= m \left[\sqrt{1 + (p/m)^2} - 1 \right] \tag{66}$$

$$= m \left[\frac{1}{2}(p/m)^2 - \frac{1}{8}(p/m)^4 + O((p/m)^6) \right]. \tag{67}$$

Thus, the next order relativistic correction to H_0 is

$$H_r = -\frac{1}{8} \frac{p^4}{m^3}. \tag{68}$$

Following the hint, notice that $p^4 = 4m^2(H_0 - V)^2$, where $V = -e^2/r$. Thus, the perturbation Hamiltonian may be written

$$H_r = -\frac{1}{2m} (H_0 - V)^2 = -\frac{1}{2m} (H_0^2 - H_0V - VH_0 + V^2). \tag{69}$$

To determine how the energy levels change in first order perturbation theory, we take the expectation value of H_r with respect

to the unperturbed stationary state wave functions:

$$E_r = \langle \psi_{n\ell m} | H_r | \psi_{n\ell m} \rangle \quad (70)$$

$$= -\frac{1}{2m} \langle \psi_{n\ell m} | H_0^2 - H_0 V - V H_0 + V^2 | \psi_{n\ell m} \rangle \quad (71)$$

$$= -\frac{1}{2m} \left[E_n^2 + 2E_n e^2 \left\langle \frac{1}{r} \right\rangle + e^4 \left\langle \frac{1}{r^2} \right\rangle \right] \quad (72)$$

$$= -\frac{1}{2m} \left[E_n^2 + 2E_n e^2 \left\langle \frac{1}{r} \right\rangle + e^4 \left\langle \frac{1}{r^2} \right\rangle \right]. \quad (73)$$

- (b) Now apply your formula to obtain the first-order relativistic kinetic energy correction to the ground state energy of hydrogen. Express your answer as a multiple of the unperturbed ground state energy, and also calculate the size of the correction in eV.

Solution: The ground state wave function of hydrogen is:

$$\psi_{100}(\mathbf{x}) = \frac{2}{\sqrt{4\pi a_0^3}} e^{-r/a_0} \quad (74)$$

As there is no dependence anywhere on the angular coordinates, we are interested in the radial wave function

$$R_{10}(r) = \frac{2}{\sqrt{a_0^3}} e^{-r/a_0}. \quad (75)$$

Let us evaluate the integral:

$$I_k \equiv \int_0^\infty x^k e^{-x} dx, \quad k \geq 0 \quad (76)$$

$$= \lim_{a \rightarrow 1} (-)^k \frac{d^k}{dx^k} \int_0^\infty e^{-ax} dx \quad (77)$$

$$= k!. \quad (78)$$

Thus, in the hydrogen atom ground state:

$$\left\langle \frac{1}{r^k} \right\rangle = \frac{4}{a_0^3} \int_0^\infty \frac{1}{r^k} e^{-2r/a_0} r^2 dr \quad (79)$$

$$= \frac{1}{2} \left(\frac{2}{a_0} \right)^k (2-k)!, \quad k \leq 2 \quad (80)$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0} \quad (81)$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{2}{a_0^2} \quad (82)$$

Thus, the first-order relativistic energy correction to the ground state energy of hydrogen is (noting that $E_0 = -\frac{1}{2}m\alpha^2$ is the unperturbed ground state energy, and that $a_0 = 1/m\alpha$):

$$E_r = -\frac{1}{2m} \left(E_0^2 + 2E_0e^2 \frac{1}{a_0} + e^4 \frac{2}{a_0^2} \right) \quad (83)$$

$$= -\frac{1}{2m} \left(\frac{1}{4}m^2\alpha^4 - m^2\alpha^4 + 2m^2\alpha^4 \right) \quad (84)$$

$$= -\frac{5}{4}\alpha^2 \left(\frac{1}{2}m\alpha^2 \right) = \frac{5}{4}\alpha^2 E_0 \quad (85)$$

$$= 0.91 \text{ meV}. \quad (86)$$

7. Let us consider an example of the use of degenerate stationary state perturbation theory. Thus, let us take the hydrogen atom, with unperturbed Hamiltonian $H_0 = \frac{P^2}{2m} - \frac{\alpha}{r}$, and consider the effect of putting this atom in a uniform external electric field: $\mathbf{E} = E\hat{e}_z$. We are interested in calculating, to first order in perturbation theory, the shifts in the $n = 2$ energy levels. Note that the $n = 2$ level is four-fold degenerate, corresponding to the eigenstates: $|2S_0\rangle, |2P_1\rangle, |2P_0\rangle, |2P_{-1}\rangle$, neglecting spins.

- (a) Write down the perturbing potential, V . [Note that we need only consider the electron's coordinates, relative to the nucleus – why?] Calculate the commutator $[V, L_z]$, and hence determine the matrix elements of V between states with different eigenvalues of L_z .

Solution: We are interested in computing the shift in the $n = 2$ energy levels (note that n is the principal quantum number here). These energy levels are computed with the center-of-mass motion separated out. Since the hydrogen atom is neutral, there is no effect on the center-of-mass motion of turning on this electric field. Hence, we only need consider the relative motion between the electron and the nucleus. Effectively, we have an electric dipole interacting with the electric field. The perturbing potential is

$$V(\mathbf{x}) = -eEz = -eEr \cos \theta. \quad (87)$$

The commutator $[V, L_z] = -eE[z, xp_y - yp_x] = 0$. Hence,

$$0 = \langle \ell' m' | [V, L_z] | \ell m \rangle = -eE(m - m') \langle \ell' m' | z | \ell m \rangle. \quad (88)$$

Thus, $\langle \ell' m' | V | \ell m \rangle = \delta_{m m'} \langle \ell' m | V | \ell m \rangle$, that is, the matrix element is zero unless $m = m'$.

- (b) You should have found a “selection rule” which simplifies the problem. What is the degeneracy that needs to be addressed in the problem now that you have made this calculation?

Solution: The degeneracy that concerns us is the one between states with like eigenvalues of L_z . These are the states $|2S_0\rangle$ and $|2P_0\rangle$.

- (c) Using the invariance of the hydrogen atom Hamiltonian under parity, write down the remaining matrix elements of V which need to be determined, and compute their values.

Solution: Because $V = eEr \cos \theta$ is odd under parity, the expectation value of V is zero between states of like parity. As the unperturbed Hamiltonian commutes with parity, its eigenstates may be expressed as eigenstates of parity. In particular, the P states have odd parity, and the S states have even parity. Hence the only (potentially) non-zero matrix elements of V in the four-dimensional subspace we are considering here are $\langle 2S_0 | V | 2P_0 \rangle$ and $\langle 2P_0 | V | 2S_0 \rangle$. Since our wave functions are real (by convention), these two matrix elements are equal.

The hydrogenic wave functions we need are (from solutions to problem 40):

$$\psi_{200} = \frac{1}{\sqrt{4\pi}} \frac{1}{2\sqrt{2}} \frac{1}{a_0^{3/2}} (2 - r/a_0) e^{-r/2a_0} \quad (89)$$

$$\psi_{210} = \sqrt{\frac{3}{4\pi}} \cos \theta \frac{1}{4\sqrt{6}} \frac{1}{a_0^{3/2}} 2 \frac{r}{a_0} e^{-r/2a_0}. \quad (90)$$

Recall also, from the solution to exercise 4:

$$I_k \equiv \int_0^\infty x^k e^{-x} dx, \quad k \geq 0 \quad (91)$$

$$= k!. \quad (92)$$

Thus, the desired matrix element is:

$$\langle 2P_0 | V | 2S_0 \rangle = -eE \frac{\sqrt{3}}{4\pi} \int_0^{2\pi} d\phi \int_{-1}^1 \cos^2 \theta d \cos \theta$$

$$\frac{1}{8\sqrt{3}} \frac{1}{a_0^3} \int_0^\infty r^2 dr r (2 - r/a_0) \frac{r}{a_0} e^{-r/a_0} \quad (93)$$

$$= -eE \frac{a_0}{3 \cdot 8} \int_0^\infty x^4 (2 - x) e^{-x} dx \quad (94)$$

$$= -eE \frac{a_0}{3 \cdot 8} (2 \cdot 4! - 5!) \quad (95)$$

$$= 3eEa_0. \quad (96)$$

The perturbing Hamiltonian may thus be written, in the $|2S_0\rangle, |2P_1\rangle, |2P_0\rangle, |2P_{-1}\rangle$ basis:

$$V = 3eEa_0 \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (97)$$

- (d) Now complete your degenerate perturbation theory calculation to determine the splitting of the states in the applied electric field. Calculate numerical splittings (in eV) for an applied field of 100 kV/cm. Also, estimate the “typical” electric field felt by the electron, due to the nucleus, in a hydrogen atom. Was the use of perturbation theory reasonable for this problem?

Solution: The eigenstates of the perturbing Hamiltonian are:

$$\frac{1}{\sqrt{2}}(|2S_0\rangle + |2P_0\rangle) \quad (98)$$

$$\frac{1}{\sqrt{2}}(|2S_0\rangle - |2P_0\rangle) \quad (99)$$

$$|2P_1\rangle \quad (100)$$

$$|2P_{-1}\rangle, \quad (101)$$

with eigenvalues $3eEa_0, -3eEa_0, 0, 0$, respectively. In a 100 kV/cm field,

$$3eEa_0 \sim 3 \times 100 \text{ keV/cm} \cdot 0.5 \times 10^{-8} \text{ cm} \quad (102)$$

$$= 1.5 \times 10^{-3} \text{ eV}. \quad (103)$$

The “typical” electric field felt by the electron in the field of the proton is:

$$E_p \sim \frac{e^2/r}{er} = \frac{2 \times -13.6 \text{ eV}}{e \times 0.5 \times 10^{-8} \text{ cm}} \quad (104)$$

$$\sim 5 \times 10^9 \text{ kV/cm}. \quad (105)$$

The use of perturbation theory for this problem appears justified.

8. It may happen that we encounter a situation where the eigenvalues of H_0 , call them ε_n and ε_m , are nearly, but not quite equal. In this case, we cannot use degenerate perturbation theory, and ordinary perturbation theory looks unreliable. Let us try to deal with such a situation: Suppose the two eigenstates $|n\rangle$ and $|m\rangle$ of H_0 have nearly the same energy (and all other eigenstates don't suffer this disease, for simplicity). Let $H = H_0 + V$, and write

$$V = \sum_{i,j} |i\rangle \langle i| V |j\rangle \langle j| \quad (106)$$

$$H_0 |i\rangle = \varepsilon_i |i\rangle, \quad (107)$$

where

$$\langle i|j\rangle = \delta_{ij}. \quad (108)$$

Let

$$V = V_1 + V_2, \quad (109)$$

with

$$V_1 \equiv |m\rangle \langle m| V |m\rangle \langle m| + |n\rangle \langle n| V |n\rangle \langle n| + \quad (110)$$

$$+ |m\rangle \langle m| V |n\rangle \langle n| + |n\rangle \langle n| V |m\rangle \langle m| \quad (111)$$

and V_2 is everything else.

If we can solve exactly the problem with $H_1 = H_0 + V_1$, then the troublesome $1/(\varepsilon_n - \varepsilon_m)$ terms are avoided by the exact treatment, and we may treat V_2 as a perturbation in ordinary perturbation theory (since $\langle i|V_2|j\rangle = 0$ for $i, j = n, m$). All states $|i\rangle$, $i \neq n, m$, are eigenstates of H_1 , since $V_1|i\rangle = 0$ in this case. However, $|n\rangle$ and $|m\rangle$ are not in general eigenstates of H_1 .

- (a) Solve exactly for the eigenstates and eigenvalues of H_1 , in the subspace spanned by $|n\rangle$, $|m\rangle$. Express your answer in terms of

$$\varepsilon_n, \varepsilon_m, \langle m|V|n\rangle, \langle n|V|n\rangle, \langle m|V|m\rangle.$$

(You may also use the shorthand

$$E_{n,m}^{(1)} = \varepsilon_{n,m} + \langle n, m | V | n, m \rangle$$

if you find it convenient.)

Solution: A vector $|i\rangle$ in our restricted subspace is of the form:

$$|i\rangle = \alpha|m\rangle + \beta|n\rangle, \quad (112)$$

where $|m\rangle$ and $|n\rangle$ are eigenstates of H_0 with eigenvalues ε_m and ε_n , respectively. Schrödinger's equation with Hamiltonian $H_1 = H_0 + V_1$ is:

$$\begin{pmatrix} \varepsilon_m + \langle m | V | m \rangle & \langle m | V | n \rangle \\ \langle n | V | m \rangle & \varepsilon_n + \langle n | V | n \rangle \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \quad (113)$$

We find eigenvalues E by taking the determinant:

$$\begin{vmatrix} \varepsilon_m + \langle m | V | m \rangle - E & \langle m | V | n \rangle \\ \langle n | V | m \rangle & \varepsilon_n + \langle n | V | n \rangle - E \end{vmatrix} = 0. \quad (114)$$

Letting $V_{ij} \equiv \langle i | V | j \rangle = V_{ji}^*$, we find eigenvalues E_{\pm} :

$$E_{\pm} = \frac{1}{2} \left[E_m^{(1)} + E_n^{(1)} \pm \sqrt{(E_m^{(1)} - E_n^{(1)})^2 + 4|V_{mn}|^2} \right]. \quad (115)$$

The corresponding eigenvectors are determined by:

$$E_m^{(1)}\alpha_{\pm} + V_{mn}\beta_{\pm} = E_{\pm}\alpha_{\pm} \quad (116)$$

$$E_n^{(1)}\beta_{\pm} + V_{nm}\alpha_{\pm} = E_{\pm}\beta_{\pm} \quad (117)$$

Hence,

$$\beta_{\pm} = \frac{E_{\pm} - E_m^{(1)}}{V_{mn}}\alpha_{\pm}. \quad (118)$$

Imposing the normalization $|\alpha_{\pm}|^2 + |\beta_{\pm}|^2 = 1$, and choosing α_{\pm} real and positive, we have:

$$\alpha_{\pm} = 1/\sqrt{1 + \frac{(E_{\pm} - E_m^{(1)})^2}{|V_{mn}|^2}} \quad (119)$$

$$\beta_{\pm} = 1/\sqrt{\left(\frac{V_{mn}}{|V_{mn}|}\right)^2 + \frac{V_{mn}^2}{(E_{\pm} - E_m^{(1)})^2}} \quad (120)$$

The eigenvectors are thus,

$$|\pm\rangle = \alpha_{\pm}|m\rangle + \beta_{\pm}|n\rangle. \quad (121)$$

- (b) As an application, consider an electron in a weak one-dimensional periodic potential (“lattice”) $V(x) = V(x + d)$. Assume the lattice has a size $L = Nd$, and that we have periodic boundary condition on our wave functions: $\psi(x) = \psi(x + L)$. With this boundary condition, the unperturbed wave functions are plane waves, $\psi_p(x) = \frac{1}{\sqrt{L}}e^{ipx}$, where $p = 2\pi n/L$, n =integer, and the unperturbed eigenenergies are $\varepsilon_n = \frac{p^2}{2m} = \left(\frac{2\pi n}{L}\right)^2 \frac{1}{2m}$. We expand the potential in a Fourier series:

$$V(x) = \sum_{n=-\infty}^{\infty} e^{in2\pi x/d} V_n$$

If we label our eigenfunctions by $|p\rangle = \frac{1}{\sqrt{L}}e^{2\pi i n_p x/L}$, determine all nonvanishing matrix elements of V :

$$\langle q|V|p\rangle$$

Express your answer in terms of V_n .

Solution:

$$\langle q|V|p\rangle = \sum_{n=-\infty}^{\infty} V_n \int_0^L e^{in2\pi x/d} \frac{1}{\sqrt{L}} e^{2\pi i(n_p - n_q)x/L} dx \quad (122)$$

$$= \sum_{n=-\infty}^{\infty} V_n \int_0^1 e^{i2\pi(n_p - n_q + Nn)u} du \quad (123)$$

$$= \sum_{n=-\infty}^{\infty} V_n \delta_{Nn, (n_q - n_p)}. \quad (124)$$

Thus, $\langle q|V|p\rangle \neq 0$ if and only if $(n_q - n_p)/N$ is an integer, and $V_{(n_q - n_p)/N} \neq 0$.

- (c) Suppose ε_{n_p} and ε_{n_q} are not close to each other $\forall n_q$, given some n_p . Calculate the perturbed wave function in ordinary first order perturbation theory corresponding to unperturbed wave function $\psi_p(x)$. Also, calculate the energy to 2^{nd} order. Express your answer in terms of V_n and the unperturbed energies.

Solution: The first order perturbed wave function is:

$$\Psi_p(x) = \psi_p(x) + \sum_{q \neq p} |q\rangle \frac{\langle q|V|p\rangle}{\varepsilon_{n_p} - \varepsilon_{n_q}}. \quad (125)$$

Now $\varepsilon_{n_p} - \varepsilon_{n_q} = \frac{2\pi^2}{mL^2}(n_p^2 - n_q^2)$, and $\langle q|V|p\rangle = 0$ unless $n_q = n_p + Nn$. Thus, letting $|P\rangle = \Psi_p(x)$:

$$|P\rangle = |p\rangle + \sum_{n_q=n_p+nN} |n_p + nN\rangle \frac{V_n}{\varepsilon_{n_p} - \varepsilon_{n_q}} \quad (126)$$

$$|P\rangle = |p\rangle + \sum_{n=-\infty, \neq 0}^{\infty} |n_p + nN\rangle \frac{V_n}{\varepsilon_{n_p} - \varepsilon_{n_p+nN}}. \quad (127)$$

Alternatively,

$$|P\rangle = |p\rangle + \sum_{n=-\infty, \neq 0}^{\infty} |n_p + nN\rangle \frac{V_n}{\frac{2\pi^2}{mL^2}(n_p^2 - n_q^2)} \quad (128)$$

$$= |p\rangle + \frac{md^2}{2\pi^2} \sum_{n=-\infty, \neq 0}^{\infty} |n_p + nN\rangle \frac{V_n}{(n_p^2 - n_q^2)/N^2} \quad (129)$$

$$= |p\rangle - \frac{md^2}{2\pi^2} \sum_{n=-\infty, \neq 0}^{\infty} |n_p + nN\rangle \frac{V_n}{n(n + 2n_p/N)} \quad (130)$$

$$= |p\rangle - \frac{md^2}{2\pi^2} \sum_{n=-\infty, \neq 0}^{\infty} |n_p + nN\rangle \frac{V_n}{n(n + 2n_p/N)} \quad (131)$$

$$= |p\rangle \left[1 - e^{-i2\pi n_p x/L} \frac{md^2}{2\pi^2} \sum_{n=-\infty, \neq 0}^{\infty} \frac{V_n}{n(n + 2n_p/N)} \exp i2\pi(n_p + nN)x/L \right]$$

$$= |p\rangle \left[1 - \frac{md^2}{2\pi^2} \sum_{n=-\infty, \neq 0}^{\infty} \frac{V_n}{n(n + 2n_p/N)} \exp i2\pi nx/d \right]. \quad (132)$$

The first order energy correction is

$$E_{p1} = \langle p|V|p\rangle = V_0. \quad (133)$$

The second order energy correction is

$$E_{p2} = \sum_{q \neq p} \frac{|\langle q|V|p\rangle|^2}{\varepsilon_{n_p} - \varepsilon_{n_q}} = \sum_{q \neq p} \frac{|V_n|^2}{\varepsilon_{n_p} - \varepsilon_{n_q}} \quad (134)$$

$$= - \sum_{n=-\infty, \neq 0}^{\infty} \frac{md^2}{2\pi^2} \frac{|V_n|^2}{n(n + 2n_p/N)}. \quad (135)$$

Thus, the energy to second order is:

$$E_p = \varepsilon_{n_p} + V_0 - \frac{md^2}{2\pi^2} \sum_{n=-\infty, \neq 0}^{\infty} \frac{|V_n|^2}{n(n + 2n_p/N)} \quad (136)$$

$$= \frac{2\pi^2 n_p^2}{mL^2} + V_0 - \frac{md^2}{2\pi^2} \sum_{n=-\infty, \neq 0}^{\infty} \frac{|V_n|^2}{n(n + 2n_p/N)} \quad (137)$$

- (d) What is the condition on n_p (and hence on p) so that $|p\rangle$ will be nearly degenerate in energy with another eigenstate of H_0 ?

Solution: From part (c), we see that the coefficient in the expansion for $|P\rangle$ blows up when $n + 2n_p/N = 0$, *i.e.*, at

$$n_p = -\frac{Nn}{2}, \quad n = \pm 1, \pm 2, \dots \quad (138)$$

When n_p takes on such a value, $p = 2\pi n_p/L = -\pi n/d$. This is degenerate with $q = \pi n/d = p + 2\pi n/d$.

- (e) Assume that the condition in (d) exists, and use part (a) to solve this “almost degenerate” case for the eigenenergies. Complete the graph in Fig. 1 for higher values of $|p|$.

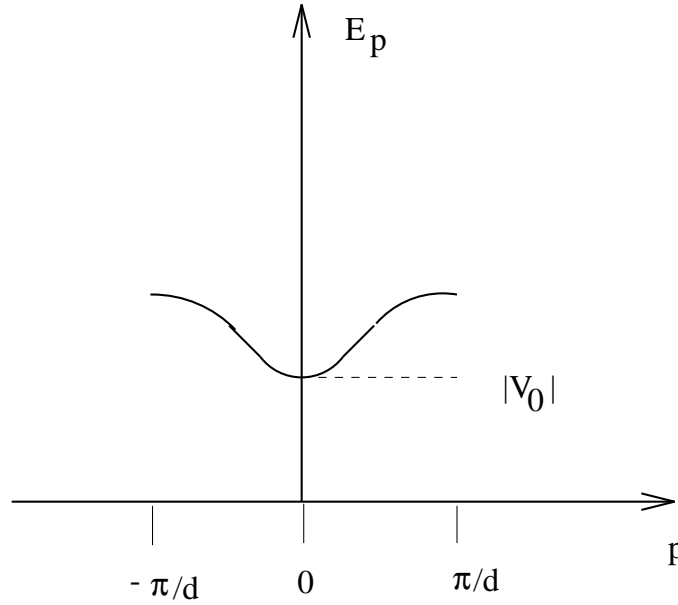


Figure 1: Energy versus momentum for the one-dimensional lattice problem (6).

Solution: Let $|p\rangle$ be nearly degenerate with $|q\rangle$:

$$p = -\frac{(n + \epsilon)\pi}{d}, \quad q = p + \frac{2\pi n}{d} = \frac{(n - \epsilon)\pi}{d}, \quad (139)$$

where $0 < |\epsilon| \ll 1$. The nearly degenerate energies are:

$$\varepsilon_{n_p} = \frac{\pi^2}{2md^2}(n + \epsilon)^2, \quad \varepsilon_{n_q} = \frac{\pi^2}{2md^2}(n - \epsilon)^2. \quad (140)$$

The matrix elements we need are:

$$\langle p|V|p\rangle = \langle q|V|q\rangle = V_0, \quad (141)$$

$$\langle p|V|q\rangle = \langle q|V|p\rangle = V_n. \quad (142)$$

The energies, using part (a), are

$$E_{\pm} = \frac{1}{2} \left[\varepsilon_{n_p} + V_0 + \varepsilon_{n_q} + V_0 \pm \sqrt{(\varepsilon_{n_p} - \varepsilon_{n_q})^2 + 4|V_n|^2} \right] \quad (143)$$

$$= \frac{\pi^2}{2md^2}(n^2 + \epsilon^2) + V_0 \pm \sqrt{\left(\frac{\pi^2 n}{md^2}\right)^2 \epsilon^2 + |V_n|^2}. \quad (144)$$

The difference in energy between these two values is

$$E_+ - E_- = 2\sqrt{\left(\frac{\pi^2 n}{md^2}\right)^2 \epsilon^2 + |V_n|^2} \quad (145)$$

$$\approx 2|V_n| + \frac{1}{|V_n|} \left(\frac{\pi^2 n}{md^2}\right)^2 \epsilon^2. \quad (146)$$

9. When we calculated the density of states for a free particle, we used a “box” of length L (in one dimension), and imposed periodic boundary conditions to ensure no net flux of particles into or out of the box. We have in mind that we can eventually let $L \rightarrow \infty$, and are really interested in quantities per unit length (or volume). Let us justify more carefully the use of periodic boundary conditions, *i.e.*, we wish to convince ourselves that the intuitive rationale given above is correct. To do this, consider a free particle in a one-dimensional “box” from $-L/2$ to $L/2$. Remembering that the Hilbert space of allowed states is a linear space, show that the periodic boundary condition:

$$\psi(-L/2) = \psi(L/2), \quad (147)$$

$$\psi'(-L/2) = \psi'(L/2) \quad (148)$$

gives acceptable wave functions. “Acceptable” here means that the probability to find a particle in the box must be constant. Are there other acceptable choices?

Solution: The Schrödinger equation for a free particle is

$$-i\partial_t\psi(x, t) = -\frac{1}{2m}\partial_x^2\psi(x, t). \quad (149)$$

We suppose that an “acceptable” wave function is one which has a constant probability to be in the “box” $(-L/2, L/2)$:

$$\frac{d}{dt} \int_{-L/2}^{L/2} |\psi(x, t)|^2 dx = 0. \quad (150)$$

It is readily verified that the function

$$\phi(x, t) = e^{i\frac{2\pi^2}{mL^2}t} \sin \frac{2\pi}{L}x \quad (151)$$

has the desired property.

If we admit $\phi(x, t)$ as an acceptable solution, and if $\psi(x, t)$ is any other acceptable solution, then $\phi + \psi$ must be acceptable, since any linear combination of acceptable solutions must be acceptable. Hence, we must have:

$$\frac{d}{dt} \int_{-L/2}^{L/2} |\psi(x, t)|^2 dx = 0; \quad (152)$$

$$\frac{d}{dt} \int_{-L/2}^{L/2} |\phi(x, t)|^2 dx = 0; \quad (153)$$

$$\frac{d}{dt} \int_{-L/2}^{L/2} |\psi(x, t) + \phi(x, t)|^2 dx = 0. \quad (154)$$

Then we may write (assuming Eqns 152 and 153):

$$0 = \frac{d}{dt} \int_{-L/2}^{L/2} [\psi(x, t)\phi^*(x, t) + \psi^*(x, t)\phi(x, t)] dx \quad (155)$$

$$= \int_{-L/2}^{L/2} \partial_t [\psi(x, t)\phi^*(x, t) + \psi^*(x, t)\phi(x, t)] dx \quad (156)$$

$$= \frac{i}{2m} \int_{-L/2}^{L/2} [(\partial_x^2\psi)\phi^* - \psi(\partial_x^2\phi) + \psi^*(\partial_x^2\phi) - (\partial_x^2\psi^*)\phi] dx \quad (157)$$

$$= \int_{-L/2}^{L/2} \partial_x [(\partial_x\psi)\phi^* - \psi(\partial_x\phi) + \psi^*(\partial_x\phi) - (\partial_x\psi^*)\phi] dx \quad (158)$$

$$= [(\partial_x\psi)\phi^* - \psi(\partial_x\phi) + \psi^*(\partial_x\phi) - (\partial_x\psi^*)\phi]_{-L/2}^{L/2}. \quad (159)$$

But $\phi(\pm L/2, t) = 0$, so

$$0 = [-\psi(\partial_x \phi^*) + \psi^*(\partial_x \phi)]_{-L/2}^{L/2}. \quad (160)$$

Further, since

$$\partial_x \phi(\pm L/2, t) = -\frac{2\pi}{L} e^{i\frac{2\pi^2}{mL^2}t}, \quad (161)$$

we obtain

$$0 = \psi(L/2, t) e^{-i\frac{2\pi^2}{mL^2}t} - \psi(-L/2, t) e^{-i\frac{2\pi^2}{mL^2}t} + \psi^*(L/2, t) e^{i\frac{2\pi^2}{mL^2}t} - \psi^*(-L/2, t) e^{i\frac{2\pi^2}{mL^2}t}. \quad (162)$$

This must be true for all times; also if ψ is acceptable, then $e^{i\theta}\psi$ must be acceptable, for real θ . Hence, ψ is acceptable if and only if Eqn. 152 holds, and:

$$\psi(L/2, t) = \psi(-L/2, t). \quad (163)$$

We note that the function $e^{i\frac{2\pi^2}{mL^2}t} \cos \frac{2\pi}{L}x$ satisfies these criteria. Thus, we could also have picked

$$\phi(x, t) = e^{i\frac{2\pi^2}{mL^2}t} \cos \frac{2\pi}{L}x \quad (164)$$

as an acceptable solution. Then the same argument reveals that any other acceptable solution ψ must satisfy the boundary condition:

$$\partial_x \psi(L/2, t) = \partial_x \psi(-L/2, t). \quad (165)$$

We finally remark that the set of functions $\left\{ e^{i\frac{n^2 2\pi^2}{mL^2}t} \sin \frac{2\pi n}{L}x, e^{i\frac{n^2 2\pi^2}{mL^2}t} \cos \frac{2\pi n}{L}x; n = 0, 1, \dots \right\}$ is a complete set of functions with the required boundary conditions.

10. See if you can generalize the result for the first Born approximation:

$$\frac{d\sigma}{d\Omega'} = \frac{m^2}{(2\pi)^2} |\hat{V}(\mathbf{p}' - \mathbf{p})|^2. \quad (166)$$

to the case where the scattered particle (mass m_f) may have a different mass than the incident particle (mass m_i).

Solution:

$$\frac{d\sigma}{d\Omega'} = \frac{m_i m_f p_f}{(2\pi)^2 p_i} |\hat{V}(\mathbf{p}_f - \mathbf{p}_i)|^2. \quad (167)$$

11. We consider the potential (called the “Yukawa potential”):

$$V(\mathbf{x}) = \frac{K e^{-\mu r}}{r}, \quad r = |\mathbf{x}|,$$

with real parameters K and $\mu > 0$. The parameter K can be regarded as the “strength” of the potential (“interaction”), and $\frac{1}{\mu}$ is effectively the “range” of distance over which the potential is important. μ itself has units of mass – note that as $\mu \rightarrow 0$ we obtain the Coulomb potential: μ can be thought of as the mass of an “exchanged particle” which mediates the force. In electromagnetism, this is the photon, hence $\mu \rightarrow m_\gamma = 0$

- (a) Find a condition on K and μ which guarantees that there are at least n bound states in this potential. You will likely fashion and use some kind of “comparison” theorem in arriving at your result. You should give at least a “heuristically convincing” argument, if you don’t actually prove it.

Solution: We assume $K < 0$, so that the potential is attractive. Consider

$$D(r) \equiv K \left(\frac{e^{-\mu r}}{r} - \frac{1}{r} \right). \quad (168)$$

For $r > 0$, $0 < e^{-\mu r} \leq 1$, hence $0 \leq D(r)$. Also

$$\frac{dD(r)}{dr} = -\frac{K}{r^2} [(1 + \mu r)e^{-\mu r} - 1] < 0. \quad (169)$$

Hence, $D(r)$ decreases monotonically for $r > 0$, with a maximum at $r = 0$:

$$\lim_{r \rightarrow 0} D(r) = -K\mu. \quad (170)$$

Thus, $0 \leq D(r) \leq -K\mu$.

We may write

$$V(r) = \frac{K}{r} + K \left(\frac{e^{-\mu r}}{r} - \frac{1}{r} \right). \quad (171)$$

Hence, $E \leq E(\text{hydrogen}) + (-K\mu)$. So, the n th level of V is a bound state, $E_n < 0$, if

$$E_n(\text{hydrogen}) - K\mu < 0 \quad (172)$$

$$-\frac{mK^2}{2n^2} - K\mu < 0 \quad (173)$$

$$-\frac{\mu}{K} < \frac{m}{2n^2}. \quad (174)$$

- (b) Using the Born approximation for the differential cross section that we developed in our discussion of time-dependent perturbation theory, calculate the differential cross section, $\frac{d\sigma}{d\Omega}$, for scattering on this potential. Consider the limit $\mu \rightarrow 0$ and compare with the Coulomb differential cross section we obtained in the notes.

Solution:

$$\hat{V}(\mathbf{p}) = \frac{4\pi K}{\mu^2 + \mathbf{p}^2}. \quad (175)$$

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{(2\pi)^2} |V(\mathbf{p}' - \mathbf{p})|^2 = \frac{4m^2 K^2}{\left(\mu^2 + 4p^2 \sin^2 \frac{\theta}{2}\right)^2}. \quad (176)$$

- (c) Integrate your differential cross section over all solid angles to obtain the “total cross section”. Again, consider the limit $\mu \rightarrow 0$. Hence, what is the total cross section for scattering on a Coulomb potential?

Solution:

$$\sigma_T = \frac{16\pi m^2 K^2}{\mu^2(\mu^2 + 4p^2)}. \quad (177)$$