

**Physics 125c**  
**Course Notes**  
**Approximate Methods**  
**040415 F. Porter**

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## 1 Introduction

Typically, problems in quantum mechanics are difficult to solve exactly with analytic methods. We thus resort to approximate methods, or to numerical methods. In this note, I review several approximate approaches.

## 2 Variational Method

There are many applications of the technique of varying quantities to find a useful extremum. This is the gist of the “variational method”. As a means of finding approximate solutions to the Schrödinger equation, a common approach is to guess an approximate form for a solution, parameterized in some way. The parameters are varied until an extremum is found. We illustrate this approach with examples.

### 2.1 Bound on Ground State Energy

Given a system with Hamiltonian  $H$ , and ground state energy  $E_0$ , we may note that for any state vector  $|\psi\rangle$  we must have:

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0. \quad (1)$$

This suggests that we may be able to use some set of functions  $\psi$ , parameterized in some way, to obtain an upper limit on the ground state energy, even if we cannot solve the problem exactly. With careful choice of “trial” function, we may even be able to get a good approximation to the energy level. Thus, the program is to find the minimum of the quantity in Eqn. 1 over variations in the parameter space to get a “least” upper bound on  $E_0$  for our trial wave functions:

$$\delta \frac{\langle\psi_{\{\boldsymbol{\theta}\}}|H|\psi_{\{\boldsymbol{\theta}\}}\rangle}{\langle\psi_{\{\boldsymbol{\theta}\}}|\psi_{\{\boldsymbol{\theta}\}}\rangle} = 0. \quad (2)$$

Here, the parameter set to be varied is denoted  $\{\boldsymbol{\theta}\}$ .

## 2.2 Example: Helium Atom

The Coulombic Hamiltonian for the helium atom is:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2\alpha}{|\mathbf{x}_1|} - \frac{2\alpha}{|\mathbf{x}_2|} + \frac{\alpha}{|\mathbf{x}_1 - \mathbf{x}_2|} \quad (3)$$

$$= -\frac{1}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2\alpha}{|\mathbf{x}_1|} - \frac{2\alpha}{|\mathbf{x}_2|} + \frac{\alpha}{|\mathbf{x}_1 - \mathbf{x}_2|}, \quad (4)$$

where  $\alpha = e^2$ ,  $m$  is the mass of the electron, and we are neglecting the motion of the nucleus. Let

$$r_1 = |\mathbf{x}_1|, \quad (5)$$

$$r_2 = |\mathbf{x}_2|, \quad (6)$$

$$r_{12} = |\mathbf{x}_1 - \mathbf{x}_2|. \quad (7)$$

Toward guessing a “good” trial wave function, note that, if the interaction term  $\alpha/r_{12}$  were not present, the ground state wave function would be simply a product of two hydrogenic ground state wave functions in  $\mathbf{x}_1$  and  $\mathbf{x}_2$ :

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0}(r_1+r_2)}, \quad a_0 = \frac{1}{m\alpha}. \quad (8)$$

There is no reason to expect that the  $\alpha/r_{12}$  term to be especially “small” compared with the other terms, so the perturbation theory approach (discussed later) may not work especially well here. However, let us use the above wave function here in the variational method, and let  $Z$  be a variable parameter, to get an upper bound on the helium ground state energy.

We need to evaluate the expectation value of  $H$ . The kinetic energy of one electron is:

$$\begin{aligned} \langle \psi | \frac{p_1^2}{2m} | \psi \rangle &= \int_{(\infty)} d^3(\mathbf{x}_1) \frac{Z^3}{\pi a_0^3} e^{-Zr_1/a_0} \frac{p_1^2}{2m} e^{-Zr_1/a_0} \\ &\quad \int_{(\infty)} d^3(\mathbf{x}_2) \frac{Z^3}{\pi a_0^3} e^{-2Zr_2/a_0} \end{aligned} \quad (9)$$

$$= Z^2 \times \text{kinetic energy of hydrogen atom ground state} \quad (10)$$

$$= Z^2 \frac{1}{2} m \alpha^2. \quad (11)$$

Thus,

$$\langle \psi | \frac{p_1^2}{2m} + \frac{p_2^2}{2m} | \psi \rangle = Z^2 m \alpha^2. \quad (12)$$

Similarly,

$$\begin{aligned}\langle\psi|\frac{2\alpha}{r_1}|\psi\rangle &= 2Z \times \text{potential energy of hydrogen atom ground state} \\ &= -2Zm\alpha^2.\end{aligned}\tag{13}$$

A remark is in order: The “2” on the left hand side is for the Coulomb potential felt by electron number one in the  $Z = 2$  field of the helium nucleus. Note that this “2” is from the Hamiltonian for helium - it is *not* a variational parameter. The factor of  $Z$  that appears on the right side *is* a variational parameter, since it arises from the trial wave function ( $\langle 1/r_1 \rangle = Z/a_0$ ). Thus, we so far have:

$$\langle\psi|\frac{1}{2m}(p_1^2 + p_2^2) - 2\alpha\left(\frac{1}{|\mathbf{x}_1|} + \frac{1}{|\mathbf{x}_2|}\right)|\psi\rangle = \frac{1}{2}m\alpha^2(2Z^2 - 8Z).\tag{14}$$

It remains to evaluate the “interaction energy” between the two electrons, for our trial wave function:

$$\langle\psi|\frac{\alpha}{r_{12}}|\psi\rangle = \alpha \int_{(\infty)} \int_{(\infty)} d^3(\mathbf{x}_1)d^3(\mathbf{x}_2) \left(\frac{Z^3}{\pi a_0^3}\right)^2 \frac{e^{-\frac{2Z}{a_0}(r_1+r_2)}}{|\mathbf{x}_1 - \mathbf{x}_2|}.\tag{15}$$

Let us digress for a moment here to obtain a couple of handy integrals.

**Theorem:** Let  $u$ ,  $v$ , and  $w$  be three positive real numbers (one of which may also be zero). Then

1.

$$\begin{aligned}I(u, v; \mathbf{x}, \mathbf{x}') &\equiv \int_{(\infty)} d^3(\mathbf{y}) \frac{\exp(-u|\mathbf{y} - \mathbf{x}| - v|\mathbf{y} - \mathbf{x}'|)}{|\mathbf{y} - \mathbf{x}||\mathbf{y} - \mathbf{x}'|} \\ &= \frac{4\pi(e^{-v\Delta} - e^{-u\Delta})}{\Delta(u^2 - v^2)},\end{aligned}\tag{16}$$

where  $\Delta \equiv |\mathbf{x} - \mathbf{x}'|$ .

2.

$$\begin{aligned}J(u, v, w) &\equiv \int_{(\infty)} d^3(\mathbf{x}) \int_{(\infty)} d^3(\mathbf{y}) \frac{\exp(-u|\mathbf{x}| - v|\mathbf{y}| - w|\mathbf{x} - \mathbf{y}|)}{|\mathbf{x}||\mathbf{y}||\mathbf{x} - \mathbf{y}|} \\ &= \frac{(4\pi)^2}{(u+v)(v+w)(w+u)}.\end{aligned}\tag{17}$$

**Proof:** (sketch)

1. Let  $\mathbf{z} = \mathbf{y} - \mathbf{x}$ , and let  $|\mathbf{z}| = r$ . Then we may make the replacement

$$d^3(\mathbf{y}) \rightarrow d^3(\mathbf{z}) = r^2 dr d\cos\theta d\phi. \quad (18)$$

Pick the 3-axis to be along  $\mathbf{x} - \mathbf{x}'$  for the integration over angles:

$$|\mathbf{y} - \mathbf{x}'| = |\mathbf{z} + \mathbf{x} - \mathbf{x}'| = \sqrt{r^2 + \Delta^2 + 2r\Delta \cos\theta}. \quad (19)$$

Thus,

$$I(u, v; \mathbf{x}, \mathbf{x}') = 2\pi \int_0^\infty r e^{-ur} dr \int_{-1}^1 d\cos\theta \frac{\exp(-v\sqrt{r^2 + \Delta^2 + 2r\Delta \cos\theta})}{\sqrt{r^2 + \Delta^2 + 2r\Delta \cos\theta}}. \quad (20)$$

Integrating over  $\cos\theta$  yields

$$I(u, v; \mathbf{x}, \mathbf{x}') = \frac{2\pi}{v\Delta} \int_0^\infty dr e^{-ur} [e^{-v|r-\Delta|} - e^{-v(r+\Delta)}]. \quad (21)$$

Finally, integrate over  $r$  to obtain

$$I(u, v; \mathbf{x}, \mathbf{x}') = \frac{4\pi (e^{-v\Delta} - e^{-u\Delta})}{\Delta(u^2 - v^2)}. \quad (22)$$

2. Let  $x = |\mathbf{x}|$ ,  $y = |\mathbf{y}|$ , and write:

$$J(u, v, w) = 4\pi \int_0^\infty x^2 dx 2\pi \int_0^\infty y^2 dy \int_{-1}^1 d\cos\theta \frac{\exp(-ux - vy - w\sqrt{x^2 + y^2 - 2xy \cos\theta})}{xy\sqrt{x^2 + y^2 - 2xy \cos\theta}}. \quad (23)$$

The integration then proceeds similarly as above.

We apply this theorem now to our problem.

$$\begin{aligned} \langle \psi | \frac{\alpha}{r_{12}} | \psi \rangle &= \alpha \left( \frac{Z^3}{\pi a_0^3} \right)^2 \int_{(\infty)} \int_{(\infty)} d^3(\mathbf{x}) d^3(\mathbf{y}) \frac{e^{-\frac{2Z}{a_0}(|\mathbf{x}|+|\mathbf{y}|)}}{|\mathbf{x} - \mathbf{y}|} \\ &= \alpha \left( \frac{Z^3}{\pi a_0^3} \right)^2 \partial_u \partial_v J(u = 2Z/a_0, v = 2Z/a_0, 0) \end{aligned} \quad (24)$$

$$= \frac{1}{2} m \alpha^2 \frac{5}{4} Z. \quad (25)$$

Thus,

$$\langle \psi | H | \psi \rangle = \frac{1}{2} m \alpha^2 \left( 2Z^2 - \frac{27}{4} Z \right). \quad (26)$$

The minimum is at  $Z = 27/16$ . Hence

$$\langle \psi | H | \psi \rangle_{\min} = -\frac{1}{2} m \alpha^2 \left[ 2 \left( \frac{27}{16} \right)^2 \right] \quad (27)$$

$$= -77.0 \text{ eV}. \quad (28)$$

Experimentally, the ground state energy of helium, from the first and second ionization energies, is

$$E_0 = -(24.59 + 54.41) = -79.00 \text{ eV}. \quad (29)$$

We have come within about 2.5% of the right value by our variational method with the “hydrogen” trial function. More careful variational calculations give good agreement. Note that the best value was obtained for  $Z = 27/16$  instead of  $Z = 2$ . This is suggestive of the “screening” of the nucleus from each electron by the other electron, reducing the effective charge by  $\frac{5}{16}e$ .

### 2.3 Other Applications of Variational Method

We may derive other potentially useful relations in connection with the variational approach. For example, let  $\{\psi_n | n = 0, 1, 2, \dots\}$  be an orthonormal set of *true* eigenfunctions of  $H$ ,  $H\psi_n = E_n\psi_n$ , with  $E_0 < E_1 \leq \dots$ . Then we can expand our trial wave function (assumed to be normalized) in this basis:

$$\psi = \sum_{n=0}^{\infty} c_n \psi_n. \quad (30)$$

We then obtain the bound:

$$\langle \psi | H | \psi \rangle = |c_0|^2 E_0 + \sum_{n=1}^{\infty} |c_n|^2 E_n \quad (31)$$

$$\geq |c_0|^2 E_0 + E_1 \sum_{n=1}^{\infty} |c_n|^2 \quad (32)$$

$$\geq (1 - |c_0|^2)(E_1 - E_0) + E_0. \quad (33)$$

Thus,

$$1 - |c_0|^2 = 1 - |\langle \psi | \psi_0 \rangle|^2 \leq \frac{\langle \psi | H | \psi \rangle - E_0}{E_1 - E_0}, \quad (34)$$

giving us a bound on how close our trial wave function is to the true ground state wave function. Of course, this is useful only if we have sufficient knowledge of the spectrum.

Likewise, we can obtain a lower bound on  $E_0$ :

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

$$E_0 \leq \langle \psi | H | \psi \rangle \leq E_1, \quad (35)$$

then

$$E_0 \geq \langle \psi | H | \psi \rangle - \frac{\langle H \psi | H \psi \rangle - \langle \psi | H | \psi \rangle^2}{E_1 - \langle \psi | H | \psi \rangle}. \quad (36)$$

The proof of this will be left to the reader. To use this theorem, a lower bound on  $E_1 - \langle \psi | H | \psi \rangle$  may be inserted.

## 2.4 Variational Theorem

We may put our intuition on a firmer foundation with the following ‘‘Variational Theorem’’:

**Theorem:** Let  $\psi \in \mathcal{H}$  (such that  $0 < \langle \psi | \psi \rangle < \infty$ ), and define the following functional on  $\mathcal{H}$ :

$$E(\psi) \equiv \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (37)$$

where  $H$  is the Hamiltonian operator, with a discrete spectrum. Then, any vector  $\psi$  for which the variation of  $E$  is stationary [that is,  $\delta E(\psi) = 0$ ] is an eigenvector in the discrete spectrum of  $H$ , and the corresponding eigenvalue of  $H$  is  $E(\psi)$ .

**Proof:** Write:

$$E(\psi) \langle \psi | \psi \rangle = \langle \psi | H | \psi \rangle. \quad (38)$$

Take the variation of both sides:

$$\delta E \langle \psi | \psi \rangle + E \langle \delta \psi | \psi \rangle + E \langle \psi | \delta \psi \rangle = \langle \delta \psi | H | \psi \rangle + \langle \psi | H | \delta \psi \rangle. \quad (39)$$

Thus,

$$\langle \psi | \psi \rangle \delta E = \langle \delta \psi | H - E | \psi \rangle + \langle \psi | H - E | \delta \psi \rangle. \quad (40)$$

If  $(H - E)|\psi\rangle = 0$ , then  $\delta E = 0$ , that is, if  $\psi$  is an eigenstate of  $H$  with eigenvalue  $E(\psi)$ , then  $E$  is stationary. Suppose, instead, that  $\delta E = 0$ . In this case,

$$\langle \delta \psi | H - E | \psi \rangle + \langle \psi | H - E | \delta \psi \rangle = 0. \quad (41)$$

Note that  $\psi$  is complex, and the variation of the real and imaginary parts are independent (the normalization is not constrained). We may deal with this by considering the variation of  $i\psi$ . If  $\delta E = 0$ , we have:

$$\langle \delta(i\psi) | H - E | \psi \rangle + \langle \psi | H - E | \delta(i\psi) \rangle = 0. \quad (42)$$

Hence,

$$-i\langle \delta(\psi) | H - E | \psi \rangle + i\langle \psi | H - E | \delta(\psi) \rangle = 0. \quad (43)$$

Combining with Eq. 41, we obtain:

$$\langle \delta \psi | H - E | \psi \rangle = 0 \quad (44)$$

$$\langle \psi | H - E | \delta \psi \rangle = 0. \quad (45)$$

This must hold for all variations  $\delta\psi$ , implying that:

$$H|\psi\rangle = E|\psi\rangle, \quad (46)$$

completing the proof.

## 2.5 The ‘‘Ritz Variational Method’’

We can modify our notion of taking a single trial wave function, with parameters to be varied, to a set of orthonormal trial wave functions. In particular, we could try to use an orthonormal set of solutions to a simpler, but preferably related, problem.

Consider a finite set of such functions:

$$\{|n\rangle : n = 0, 1, 2, \dots, N\}. \quad (47)$$

Our trial wave function is constructed according to:

$$|\psi\rangle = \sum_{n=0}^N a_n |n\rangle. \quad (48)$$



The  $a_n$  are  $N + 1$  complex parameters to be varied. Let us impose the normalization constraint

$$\sum_{n=0}^N |a_n|^2 = 1, \quad (49)$$

so that  $\langle \psi | \psi \rangle = 1$ .

We wish to find the parameters such that the variation of the expectation of  $H$  vanishes:

$$\delta(\langle \psi | H | \psi \rangle) = 0, \quad (50)$$

subject to the constraint 49. Thus,

$$0 = \delta \left( \sum_{\substack{n=0 \\ m=0}}^N \langle \psi | m \rangle \langle m | H | n \rangle \langle n | \psi \rangle \right) \quad (51)$$

$$= \delta \left( \sum_{\substack{n=0 \\ m=0}}^N a_m^* a_n \langle m | H | n \rangle \right), \quad (52)$$

subject to

$$0 = \delta(1) = \delta \left( \sum_{n=0}^N |a_n|^2 \right) = \delta \left( \sum_{\substack{n=0 \\ m=0}}^N a_m^* a_n \delta_{mn} \right). \quad (53)$$

We may impose the constraint with the method of Lagrange multipliers:

$$0 = \delta \left( \sum_{m,n} a_m^* a_n \langle m | H | n \rangle \right) - \delta \left( \lambda \sum_{m,n} a_m^* a_n \delta_{mn} \right) \quad (54)$$

$$= \sum_{m,n} [\delta a_m^* a_n (\langle m | H | n \rangle - \lambda \delta_{mn}) + a_m^* \delta a_n (\langle m | H | n \rangle - \lambda \delta_{mn})] \quad (55)$$

$$= \sum_{m,n} [\delta a_m^* a_n (\langle m | H | n \rangle - \lambda \delta_{mn}) + \delta a_m a_n^* (\langle m | H | n \rangle^* - \lambda \delta_{mn})], \quad (56)$$

where the last equation was obtain via a relabeling of the  $m, n$  indices. As in the previous section, we note that the real and imaginary parts may be varied separately, and hence:

$$\sum_{m,n} \delta a_m^* a_n (\langle m | H | n \rangle - \lambda \delta_{mn}) = 0, \quad (57)$$

$$\sum_{m,n} \delta a_m a_n^* (\langle m | H | n \rangle^* - \lambda \delta_{mn}) = 0. \quad (58)$$

We may also vary each of the individual  $a_n$ 's separately, setting all  $\delta a_n = 0$  except for one. This gives:

$$\sum_n a_n (\langle m|H|n\rangle - \lambda\delta_{mn}) = 0. \quad (59)$$

This may be rewritten, in our finite basis:

$$\langle m| \left[ \sum_n a_n (H - \lambda I) |n\rangle \right] = 0, \quad \text{or} \quad (60)$$

$$\langle m| (H - \lambda I) \sum_n a_n |n\rangle = 0, \quad \forall m. \quad (61)$$

That is,  $\sum_n a_n^{(i)} |n\rangle$ ,  $i = 0, 1, \dots, N$  are eigenvectors of  $H$ , in this reduced basis, with eigenvalues  $\lambda^{(i)}$ .

If we managed to pick “good” functions  $|n\rangle$ , then the first few  $E^{(i)} = \lambda^{(i)}$  may be good approximations to the first few energy levels of the full problem.

### 3 The WKB Approximation

The WKB (for Wentzel-Kramers-Brillouin) method makes use of the wave nature of the solutions to the Schrödinger equation between classical turning points. We'll give a simple-minded treatment here; refinements are possible.

We wish to consider the problem of stationary states in a one-dimensional potential well (or equivalent one-dimensional potential for three-dimensional problems with spherical symmetry). Label the states by  $n$ , where  $n = 0, 1, \dots$ , and  $E_0 < E_1 < \dots$ . Consider  $E_n$ , with classical turning points  $x_1, x_2$ . The energy  $E_n$  corresponds to the  $(n+1)$ th state, or the  $n^{\text{th}}$  “excited state.” The wave function will be oscillatory, with roughly  $n+1$  half-waves between the classical turning points. Fig. 1 illustrates this for the fourth excited state.

Let's see how we can use this idea to estimate the energy levels. Consider an oscillatory solution of the form:

$$\psi(x) = A(x) \sin \phi(x), \quad (62)$$

where  $A(x) > 0$ , and  $\phi(x)$  is a phase increasing monotonically with  $x$ . Whenever  $\phi(x) = k\pi$ , where  $k$  is an integer, there is a node in  $\psi(x)$ . Consider the change in  $\phi$  between turning points:

$$\Delta\phi = \phi(x_2) - \phi(x_1). \quad (63)$$

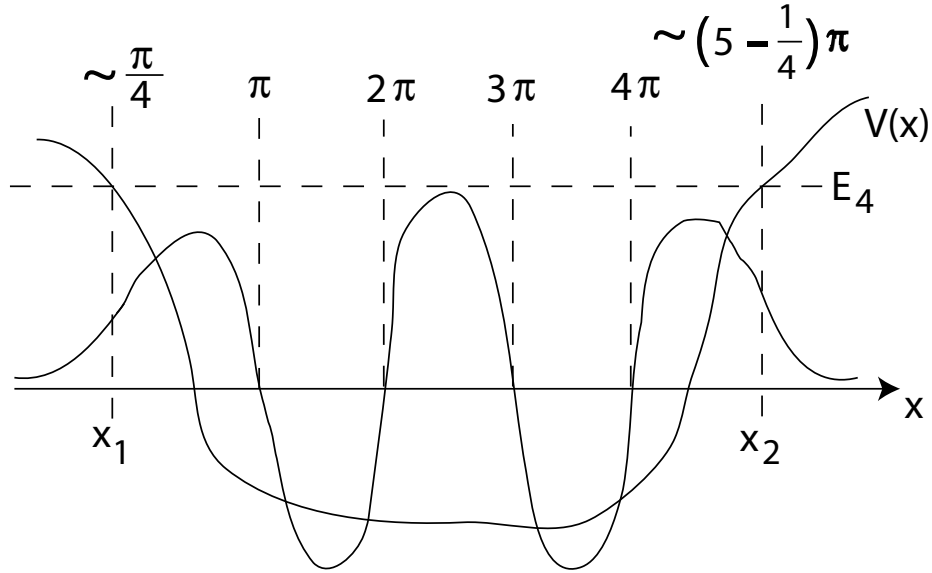


Figure 1: Illustration of the WKB method. The classical turning points  $x_1$  and  $x_2$  are shown for the fourth excited state with energy  $E_4$ . The phase is counted between the turning points.

The figure is suggestive of  $\Delta\phi \approx (n + \frac{1}{2})\pi$ . More rigorously, we may state:

$$n\pi < \Delta\phi \leq (n + 1)\pi. \quad (64)$$

It is readily seen that the right bound is achieved for an infinite square well potential. Typically, we simply make the choice  $(n + \frac{1}{2})\pi$ , although it may not be difficult to do better in some circumstances.

Now let us make an approximate calculation for this change in phase according to the Schrödinger equation. For a region of constant  $V < E_n$  the wave function is

$$\psi(x) = A \sin(x - x_0)p, \quad (65)$$

where  $A$  and  $x_0$  are constants, and

$$p = \sqrt{2m(E - V)}. \quad (66)$$

Thus, in a region of constant  $V$ , the phase varies as  $\phi(x) = (x - x_0)p$ . The change in phase as we increase  $x$  slightly is

$$d\phi = p dx = \sqrt{2m(E - V)} dx. \quad (67)$$

Adding up all such contributions between the turning points yields:

$$\Delta\phi = \int_{x_1}^{x_2} \frac{d\phi}{dx} dx \approx \int_{x_1}^{x_2} \sqrt{2m(E - V)} dx. \quad (68)$$

The approximation is better the more slowly  $V(x)$  varies with  $x$ , since we have used an integrand based on the assumption of constant  $V$  regions. Therefore, we have:

$$\int_{x_1}^{x_2} \sqrt{2m[E_n - V(x)]} dx \approx (n + \frac{1}{2})\pi. \quad (69)$$

To use this result to estimate the energy levels  $E_n$ , we must first solve for the turning points as a function of  $E$ :

$$V(x_1) = V(x_2) = E, \quad x_2 > x_1, \quad (70)$$

yielding the functions  $x_1(E)$  and  $x_2(E)$ . Next, we solve for the function of  $E$ :

$$f(E) = \int_{x_1(E)}^{x_2(E)} \sqrt{2m[E_n - V(x)]} dx. \quad (71)$$

Finally, we determine  $E_n$  as the solution to

$$f(E_n) = (n + \frac{1}{2})\pi. \quad (72)$$

This is the ‘‘WKB method’’.

### 3.1 Example: Infinite Square Well

Consider the infinite square well potential:

$$V(x) = \begin{cases} 0 & 0 < x < \Delta \\ \infty & x \leq 0 \text{ or } x \geq \Delta. \end{cases} \quad (73)$$

We have  $x_1 = 0$ , and  $x_2 = \Delta$ , independent of  $E$ . Thus,

$$f(E) = \int_0^\Delta \sqrt{2mE} dx = \sqrt{2mE}\Delta. \quad (74)$$

Letting

$$\Delta\sqrt{2mE_n} = (n + \frac{1}{2})\pi, \quad (75)$$

we obtain the result

$$E_n = \frac{(n + \frac{1}{2})^2 \pi^2}{2m\Delta^2}, \quad n = 0, 1, 2, \dots \quad (76)$$

Actually, we can do better than this. As we noted earlier, the change in phase for this potential is really  $(n + 1)\pi$ , since the turning points are nodes. Thus, we expect

$$E_n = \frac{(n + 1)^2 \pi^2}{2m\Delta^2}, \quad n = 0, 1, 2, \dots \quad (77)$$

This is, in fact, the exact result, which is to be expected, because the assumption of constant  $V$  is valid in this case.

### 3.2 Example: Harmonic Oscillator

Consider the one-dimensional simple harmonic oscillator potential:

$$V(x) = \frac{1}{2}kx^2. \quad (78)$$

Let  $\omega_0 = \sqrt{k/m}$  be the classical angular frequency. Find the turning points:

$$E = \frac{1}{2}kx_1^2 = \frac{1}{2}kx_2^2, \quad (79)$$

$$-x_1 = x_2 = x_0 \equiv \sqrt{\frac{2E}{k}}. \quad (80)$$

Now find  $f(E)$ :

$$f(E) = \int_{-x_0}^{x_0} dx \sqrt{2m[E - V(x)]} \quad (81)$$

$$= 2\sqrt{mk}x_0^2 \int_0^1 dx \sqrt{1 - x^2} \quad (82)$$

$$= 2\sqrt{mk}x_0^2 \int_0^{\pi/4} \cos^2 \theta d\theta \quad (83)$$

$$= \pi\sqrt{mk} \frac{x_0^2}{2} \quad (84)$$

$$= \pi \frac{E}{\omega_0}. \quad (85)$$

Setting  $f(E_n) = (n + \frac{1}{2})\pi$ , we arrive at the result:

$$E_n = (n + \frac{1}{2})\omega_0, \quad n = 0, 1, 2, \dots \quad (86)$$

This turns out to be the exact spectrum for the bound states of the simple harmonic oscillator potential.

## 4 Method of Stationary Phase

Suppose that we wish to evaluate an integral of the form (known as the *generalized Fourier integral*):

$$I(\epsilon) = \int_{-\infty}^{\infty} f(x)e^{i\theta(x)/\epsilon} dx, \quad (87)$$

where  $f$  and  $\theta$  are real, and  $\epsilon > 0$ . If  $\epsilon$  is very small, the phase oscillation is very rapid, and we may anticipate little contribution to the integral from such a region. The dominant contribution may be expected to arise where the phase variation is slow, that is, where  $d\theta/dx = 0$ . This is the idea behind the method of stationary phase. Figure 2 illustrates the idea.

Let us pursue this notion. Suppose  $\theta(x)$  has a (single) stationary point at  $x = x_0$ :  $\theta'(x_0) = 0$ . We do a Taylor series expansion about this point, letting  $x = x_0 + \sqrt{\epsilon}u$ :

$$I(\epsilon) = \int_{-\infty}^{\infty} \left[ f(x_0) + \sqrt{\epsilon}u f'(x_0) + \frac{1}{2}\epsilon u^2 f''(x_0) + O(\epsilon^{3/2}) \right] \exp \left\{ i \left[ \theta(x_0)/\epsilon + \frac{1}{2}u^2 \theta''(x_0) + \frac{1}{3!}\sqrt{\epsilon}u^3 \theta'''(x_0) + O(\epsilon) \right] \right\} \sqrt{\epsilon} du \quad (88)$$

$$= \sqrt{\epsilon} f(x_0) e^{i\theta(x_0)/\epsilon} \int_{-\infty}^{\infty} \left[ 1 + \sqrt{\epsilon}u \frac{f'(x_0)}{f(x_0)} + \frac{1}{2}\epsilon u^2 \frac{f''(x_0)}{f(x_0)} + O(\epsilon^{3/2}) \right] e^{\frac{i}{2}u^2 \theta''(x_0)} \exp \left[ \frac{i}{3!}\sqrt{\epsilon}u^3 \theta'''(x_0) + O(\epsilon) \right] du \quad (89)$$

$$= \sqrt{\epsilon} f(x_0) e^{i\theta(x_0)/\epsilon} \int_{-\infty}^{\infty} \left\{ 1 + \sqrt{\epsilon} \left[ u \frac{f'(x_0)}{f(x_0)} + \frac{1}{3!}u^3 \theta'''(x_0) + O(\epsilon) \right] \right\} e^{\frac{i}{2}u^2 \theta''(x_0)} du. \quad (90)$$

The terms odd in  $u$  vanish on integration, leaving:

$$I(\epsilon) = \sqrt{\epsilon} f(x_0) e^{i\theta(x_0)/\epsilon} \int_{-\infty}^{\infty} e^{\frac{i}{2}u^2 \theta''(x_0)} du$$

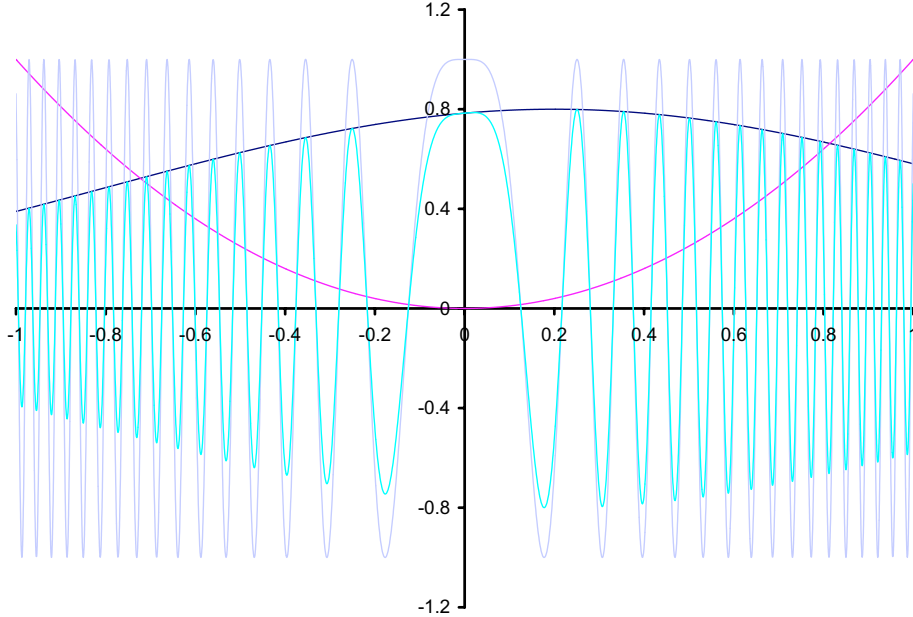


Figure 2: Illustration for the method of stationary phase. The smooth concave down curve is  $f(x)$ . The smooth concave up curve is  $\theta(x)$ . The oscillating curve of constant amplitude is the real part of  $e^{i\theta(x)/\epsilon}$ . The remaining oscillatory curve is the real part of the desired integrand:  $f(x)e^{i\theta(x)/\epsilon}$ . In this illustration,  $\epsilon = 0.01$ ,  $f(x) = 0.8 \exp\left[-\frac{1}{2}(x - 0.2)^2\right]$ , and  $\theta(x) = x^2$ .

$$= \sqrt{\epsilon} f(x_0) e^{i\theta(x_0)/\epsilon} e^{i\frac{\pi}{4} \text{sign} \theta''(x_0)} \sqrt{\frac{2\pi}{|\theta''(x_0)|}} [1 + O(\epsilon)]. \quad (91)$$

For multiple stationary points, we simply sum over this expression evaluated at each stationary point.

#### 4.1 Application: Asymptotic Bessel Function

Suppose we wish to evaluate the  $J_n(z)$  Bessel function for large  $z$ . We start with the integral representation:

$$J_n(z) = \frac{1}{i^n \pi} \int_0^\pi e^{iz \cos \phi} \cos(n\phi) d\phi. \quad (92)$$

The role of  $\epsilon$  is carried by  $1/z$ . The quantity  $\theta(\phi)$  is just  $\cos \phi$ . This has stationary points at  $\phi = 0$  and  $\phi = \pi$ , within the region of integration. There

is a potential difficulty with the fact that these points are at the limits of the integration. However, we may use the fact that the integrand is symmetric about  $\phi = 0$ , and periodic, to write:

$$J_n(z) = \frac{1}{2i^n \pi} \int_{-\pi/2}^{3\pi/2} e^{iz \cos \phi} \cos(n\phi) d\phi. \quad (93)$$

We need to sum Eqn. 91 over the two stationary points, with

$$f(0) = \cos(n0) = 1, \quad (94)$$

$$f(\pi) = \cos(n\pi) = (-1)^n, \quad (95)$$

$$\theta(0) = -\theta(\pi) = 1, \quad (96)$$

$$\theta''(0) = -\theta''(\pi) = -1. \quad (97)$$

The result is, for large  $z$ :

$$J_n(z) \sim \frac{1}{\sqrt{2\pi z}} \frac{1}{2\pi i^n} \left[ e^{i(z-\pi/4)} + (e^{i\pi})^n e^{-i(z-\pi/4)} \right] \quad (98)$$

$$= \frac{1}{\sqrt{2\pi z}} \left[ e^{i(z-n\pi/2-\pi/4)} + e^{-i(z-n\pi/2-\pi/4)} \right] \quad (99)$$

$$= \sqrt{\frac{2}{\pi z}} \cos \left( z - \frac{n\pi}{2} - \frac{\pi}{4} \right). \quad (100)$$

This is the familiar result.

The reader may wish to go back and verify that the application of Eqn. 91 is really proper, as we have violated some of the assumptions made in obtaining that result. Indeed, a more general treatment may be obtained based on the ‘‘Reimann-Lebesgue Lemma’’:

**Lemma:** Let  $|f(x)|$  be an integrable function of real variable  $x$ , and  $\theta(x)$  be a continuously differentiable real function on the interval  $[a, b]$ , except that  $\theta$  is nowhere constant on any finite subinterval of  $[a, b]$ . Then

$$I(\epsilon) \equiv \int_a^b f(x) e^{i\theta(x)/\epsilon} dx \rightarrow 0 \quad \text{as } \epsilon \rightarrow 0+. \quad (101)$$

## 4.2 Application: Quantum Mechanics of Free Particle Asymptotic Wave Function

Let’s try an application of the method of stationary phase in quantum mechanics. Consider the free particle (in one dimension), and the question:



What is the asymptotic behavior of the wave function as  $t \rightarrow \infty$ ? Suppose in particular, we are interested in a wave function which in momentum space is localized around a momentum  $q$  at time  $t = 0$ . The position space wave function at  $t = 0$  is:

$$\psi(x, 0) = \frac{1}{2\pi} \int dp \hat{\psi}(p) e^{ipx}. \quad (102)$$

Taking  $\hat{\psi}$  to be real, we find that  $|\psi(x, 0)|$  is symmetric about 0. If we further suppose that  $\hat{\psi} > 0$ , then  $|\psi|$  is maximal at  $x = 0$  (alternatively, we could choose our coordinate system such that this is the case<sup>1</sup>).

The time evolution of the wave function is:

$$\psi(x, t) = \frac{1}{2\pi} \int dp \hat{\psi}(p) e^{ipx - itp^2/2m}. \quad (103)$$

The phase of interest here is

$$\theta(p)/\epsilon = px - tp^2/2m. \quad (104)$$

This is stationary at  $p = p_0$ , where:

$$0 = \frac{1}{\epsilon} \frac{d\theta}{dp} \Big|_{p_0} = x - \frac{p_0}{m} t. \quad (105)$$

Now we use equation 91 to determine the asymptotic form of  $\psi(x, t)$  as  $t \rightarrow \infty$ , with  $\epsilon = 1/t$ . The stationary point is  $p_0 = mx/t$ , and

$$\theta(p_0) = \frac{m}{2} \frac{x^2}{t^2}, \quad (106)$$

$$\theta''(p_0) = -1/m, \quad (107)$$

$$f(p_0) = \frac{1}{2\pi} \hat{\psi}(mx/t). \quad (108)$$

Thus,

$$\psi(x, t) \rightarrow \frac{1}{\sqrt{t}} \hat{\psi}(mx/t) e^{imx^2/2t} e^{-i\pi/4} \sqrt{m/2\pi}, \quad \text{as } t \rightarrow \infty, \quad (109)$$

$$= \hat{\psi}(mx/t) \sqrt{\frac{m}{2\pi t}} e^{-i\pi/4} e^{imx^2/2t}. \quad (110)$$

---

<sup>1</sup>You may wish to recall that a translation by  $x_0$  in position corresponds to multiplication by a phase  $e^{-ipx_0}$  in momentum space

The probability density, at large times, is thus:

$$|\psi(x, t)|^2 = |\hat{\psi}(mx/t)|^2 \frac{m}{2\pi t}. \quad (111)$$

Note that this is peaked around  $x = qt/m$ , if  $\hat{\psi}(p)$  is peaked around  $q$ , giving the appropriate classical correspondence for the motion. The probability density falls as  $1/t$ , but also spreads out as  $1/t$  (due to the  $1/t$  in the argument of  $\hat{\psi}$ ). Probability is conserved:

$$\int |\psi(x, t)|^2 dx \underset{t \rightarrow \infty}{=} \int |\hat{\psi}(mx/t)|^2 \frac{m}{2\pi t} dx = \frac{1}{2\pi} \int |\hat{\psi}(p)|^2 dp = \text{constant}. \quad (112)$$

### 4.3 Application: A Scattering Problem

Let us try another example, a one-dimensional scattering problem. Suppose that there is a localized potential  $V(x)$ :

$$V(x) = 0, \quad |x| > L. \quad (113)$$

For a given (positive) momentum component, and  $x > |L|$ ,  $E = p^2/2m$ , and the wave function corresponding to this momentum is:

$$\psi_E(x) = \begin{cases} e^{ipx} + R(E)e^{-ipx}, & x < -L, \\ T(E)e^{ipx}, & x > L. \end{cases} \quad (114)$$

The solution to the time-dependent Schrödinger equation, for  $|x| > L$ , is

$$\psi(x, t) = \frac{1}{2\pi} \int dp \hat{\psi}(p) \psi_E(x) e^{-iEt}, \quad (115)$$

where we have now summed over the plane wave components to obtain a physical wave packet. Again, we assume that  $\hat{\psi}(p)$  is localized around  $p = q$ . Note that, if  $V(x) = 0$ , this is just

$$\psi(x, t) = \frac{1}{2\pi} \int dp \hat{\psi}(p) e^{ipx} e^{-ip^2 t/2m}, \quad (116)$$

as in the previous section.

Consider  $x > L$ : Let  $T(E) = |T(E)|e^{i\delta(E)}$ . Then,

$$\psi(x, t) = \frac{1}{2\pi} \int dp \hat{\psi}(p) |T(E)| e^{i\delta(E)} e^{i(px - Et)}. \quad (117)$$

The phase factor is:

$$\phi = \frac{1}{\epsilon}\theta = \delta(E) + px - Et. \quad (118)$$

This phase is stationary at  $d\phi/dp = 0$ . The solution is  $p = p_0(x, t)$ . Now, significant contributions to  $\psi(x, t)$  will only occur when  $p = p_0(x, t)$  is near  $q$ . Hence, we may approximate

$$\delta(E) \approx \delta(E_0) + (E - E_0)\tau(E_0), \quad (119)$$

where  $E_0 \equiv q^2/2m$  and  $\tau(E) \equiv \partial\delta(E)/\partial(E)$ .

Thus, our problem is to evaluate:

$$\psi(x, t) \approx e^{i\delta(E_0) - iE_0\tau(E_0)} \int \frac{dp}{2\pi} \hat{\psi}(p) |T(E)| e^{i[px - E(t - \tau(E_0))]}. \quad (120)$$

This is just like our free particle case, Eqn. 103, except  $t$  is replaced with  $t - \tau(E_0)$ . Hence, by the method of stationary phase, as  $t \rightarrow \infty$ , for  $x > L$ :

$$\psi(x, t) = \hat{\psi} \left[ m \frac{x}{t - \tau(E_0)} \right] \sqrt{\frac{m}{2\pi [t - \tau(E_0)]}} e^{-i\pi/4} e^{imx^2/2[t - \tau(E_0)]} |T(E)| e^{i[\delta(E_0) - E_0\tau(E_0)]}. \quad (121)$$

The asymptotic probability density is:

$$|\psi(x, t)|^2 = \left| \hat{\psi} \left[ m \frac{x}{t - \tau(E_0)} \right] \right|^2 \frac{m}{2\pi [t - \tau(E_0)]} \left| T \left\{ \frac{[mx/(t - \tau(E_0))]^2}{2m} \right\} \right|^2, \quad (122)$$

where we have substituted  $E = \frac{[mx/(t - \tau(E_0))]^2}{2m}$ .

This result is of the form of the free particle probability density times the transmission probability. However, the time  $t$  is replaced by  $t - \tau(E_0)$ . That is, the outgoing wave is delayed relative to free propagation ( $V = 0$ ) by a time delay given by  $\tau(E) = d\delta/dE$ . It is suggested that the reader consider the classical correspondence for this effect. We will encounter this notion again when we discuss phase shifts in scattering theory.

## 5 Stationary State Perturbation Theory

We are frequently concerned with the problem of determining the stationary state eigenvalues and eigenfunctions of the Hamiltonian. There is a relatively systematic iterative approach to solving this problem, if a suitable

first approximation can be found. This is the method of stationary state perturbation theory, which we develop with a simplified approach here.

Suppose we are given a Hamiltonian of the form  $H = H_0 + V$ , where we know the eigenfunctions and eigenvalues corresponding to  $H_0$ :

$$H_0|n\rangle = \varepsilon_n|n\rangle. \quad (123)$$

We are interested in solving, at least approximately, the problem:

$$H|N\rangle = E_N|N\rangle. \quad (124)$$

If  $V$  is “small”, we expect that  $|n\rangle$  and  $\varepsilon_n$  will be approximate eigenfunctions and eigenvalues of  $H$ . We use this idea to form an iterative expansion for  $|N\rangle$  and  $E_N$ .

We introduce a “bookkeeping” parameter,  $\lambda$ , to count powers (of  $V$ ) in the expansion. Let  $H(\lambda) \equiv H_0 + \lambda V$ . We expect the eigenstates of  $H(\lambda)$  to vary smoothly from eigenstates of  $H_0$  at  $\lambda = 0$  to eigenstates of  $H$  at  $\lambda = 1$ . Thus, consider the following series:

$$|N\rangle = |n\rangle + \lambda|N_1\rangle + \lambda^2|N_2\rangle + \dots, \quad (125)$$

$$E_n = \varepsilon_n + \lambda E_{n1} + \lambda^2 E_{n2} + \dots \quad (126)$$

Note, however, that such an expansion does not always make sense. For example, we cannot do perturbation theory on the free particle problem to solve a bound state problem, no matter how “weak” the potential.

We need to develop an algorithm to solve for the terms in the series. Assume our unperturbed system of eigenstates is orthonormal:

$$\langle n|m\rangle = \delta_{nm}. \quad (127)$$

Normalize the eigenstates of  $H$  so that:

$$\langle n|N\rangle = 1. \quad (128)$$

Assuming our perturbation is not too large, this should be possible. Of course, we won’t have  $\langle N|N\rangle = 1$  in general, and will have to renormalize these functions at the end. Then we have

$$1 = \langle n|N\rangle = \langle n|n\rangle + \lambda\langle n|N_1\rangle + \lambda^2\langle n|N_2\rangle + \dots \quad (129)$$

The coefficient of each power of  $\lambda$  must vanish, so that:

$$\langle n|N_k\rangle = 0, \quad k = 1, 2, \dots \quad (130)$$

Now consider the Schrödinger equation:

$$(H_0 + \lambda V)|N\rangle = E_N|N\rangle, \quad (131)$$

or

$$\begin{aligned} (H_0 + \lambda V)(|n\rangle + \lambda|N_1\rangle + \lambda^2|N_2\rangle + \dots) & \quad (132) \\ = (\varepsilon_n + \lambda E_{N1} + \lambda^2 E_{N2} + \dots)(|n\rangle + \lambda|N_1\rangle + \lambda^2|N_2\rangle + \dots). & \end{aligned}$$

Equating powers of  $\lambda$  on both sides, we obtain:

$$\lambda^0 : \quad H_0|n\rangle = \varepsilon_n|n\rangle \quad (133)$$

$$\lambda^1 : \quad H_0|N_1\rangle + V|n\rangle = \varepsilon|N_1\rangle + E_{N1}|n\rangle \quad (134)$$

$$\lambda^k : \quad H_0|N_k\rangle + V|N_{k-1}\rangle = \sum_{j=0}^k E_{nj}|N_{k-j}\rangle, \quad (135)$$

where

$$E_{n0} \equiv \varepsilon_n \quad (136)$$

$$|N_0\rangle \equiv |n\rangle. \quad (137)$$

Consider the  $\lambda^1$  equation, and take the scalar product with  $\langle n|$ :

$$\langle n|H_0|N_1\rangle + \langle n|V|n\rangle = \langle n|\varepsilon_n|N_1\rangle + \langle n|E_{N1}|n\rangle. \quad (138)$$

Thus, the first order correction to the  $n$ th energy level is

$$E_{N1} = \langle n|V|n\rangle. \quad (139)$$

Or, to first order in the potential  $V$  (setting  $\lambda = 1$ ):

$$E_N = \varepsilon_n + \langle n|V|n\rangle + O(V^2). \quad (140)$$

This is the most commonly used equation in stationary state perturbation theory.

In general, we find from Eqn. 135:

$$E_{nk} = \langle n|V|N_{k-1}\rangle. \quad (141)$$

If we know the  $(k - 1)$ th order correction to the wave function, we can obtain the  $k$ th order energy correction. To find the wave function corrections, expand in the eigenstates of  $H_0$ :

$$|N_k\rangle = \sum_{m \neq n} |m\rangle \langle m|N_k\rangle, \quad k = 1, 2, \dots, \quad (142)$$

where the  $m = n$  terms in the sum are excluded since  $\langle n|N_k\rangle = 0, \forall k > 0$ . Now take the scalar product of Eqn. 135 with  $\langle m|$  to get the expansion coefficients:

$$\langle m|H_0|N_k\rangle + \langle m|V|N_{k-1}\rangle = \sum_{j=0}^k E_{nj} \langle m|N_{k-j}\rangle \quad (143)$$

$$\varepsilon_m \langle m|N_k\rangle + \langle m|V|N_{k-1}\rangle = \varepsilon_n \langle m|N_k\rangle + \sum_{j=1}^{k-1} E_{nj} \langle m|N_{k-j}\rangle, \quad (144)$$

where the  $j = k$  term in the sum may be excluded, since  $\langle m|n\rangle = 0$ . Thus, if  $\varepsilon_m \neq \varepsilon_n$ :

$$\langle m|N_k\rangle = \frac{1}{\varepsilon_n - \varepsilon_m} \left( \langle m|V|N_{k-1}\rangle - \sum_{j=1}^{k-1} E_{nj} \langle m|N_{k-j}\rangle \right). \quad (145)$$

We'll try an example – estimating the helium ground state energy. Let  $H = H_0 + V$ , with

$$H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2\alpha}{r_1} - \frac{2\alpha}{r_2} \quad (146)$$

$$V = \frac{\alpha}{r_{12}}. \quad (147)$$

The ground state wave function for the unperturbed  $H_0$  is just

$$|n = 0\rangle = |0\rangle_0 = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0}(r_1+r_2)}, \quad \text{with } Z = 2. \quad (148)$$

The unperturbed ground state energy is:

$$\varepsilon_0 = -\frac{1}{2}m\alpha^2(2Z^2) = -108.9 \text{ eV}. \quad (149)$$

The first order correction to the energy is

$$E_{01} = {}_0\langle 0|V|0\rangle_0 = \int_{(\infty)} d^3(\mathbf{x}_1) \int_{(\infty)} d^3(\mathbf{x}_2) \left( \frac{Z^3}{\pi a_0^3} \right)^2 e^{-\frac{2Z}{a_0}(r_1+r_2)} \frac{\alpha}{r_{12}}. \quad (150)$$

This is an integral we already evaluated, hence

$$E_{01} = \frac{1}{2} m \alpha^2 \left( \frac{5}{4} Z \right)_{Z=2} = 34.0 \text{ eV}. \quad (151)$$

The ground state energy, to first order in perturbation theory is thus

$$E_0 = \varepsilon_0 + {}_0\langle 0|V|0\rangle_0 + O(V^2) \quad (152)$$

$$= -\frac{1}{2} m \alpha^2 \left( 2Z^2 - \frac{5}{4} Z \right) + O(V^2) \quad (153)$$

$$= -74.9 \text{ eV} + O(V^2). \quad (154)$$

Our first order perturbation theory correction to the energy is 34 eV, to be applied to the zeroth order level at -109 eV. This is a rather large correction, so it isn't surprising that the result is still 4.1 eV away from the observed value of -79.0 eV. Note that the variational calculation we performed does better – it really is the same calculation, except that there in addition we allowed  $Z$  to vary to accommodate the screening effect.

We might guess that the size of the second order effect could be estimated by squaring the size of the first order correction:

$$O(V^2) \approx 74.9 \left( \frac{34.0}{108.9} \right)^2 = 7.3 \text{ eV}. \quad (155)$$

This is certainly of the right order, but is only an order-of-magnitude estimate. To do better, we should perform the second order perturbation theory calculation:

$$E_{n2} = \langle n|V|N_1\rangle \quad (156)$$

$$= \sum_{m \neq n} \langle n|V|m\rangle \langle m|N_1\rangle \quad (157)$$

$$= \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{\varepsilon_n - \varepsilon_m}. \quad (158)$$

The second order correction depends on the “overlap” between  $\langle m|$  and  $V|n\rangle$  where  $\langle m| \neq \langle n|$ , and also on the energy level spacing in the unperturbed Hamiltonian.

## 5.1 Normalization

We chose the normalization  $\langle n|N\rangle = 1$  in order to make the expansion convenient. The drawback is that  $|N\rangle$  is not normalized to unit total probability. We may renormalize to obtain a normalized wave function as follows: Let  $|\hat{N}\rangle = \sqrt{A}|N\rangle$  such that  $\langle\hat{N}|\hat{N}\rangle = 1$ . The constant  $A = 1/\langle N|N\rangle$  is called the “wave function renormalization constant”. Take

$$\sqrt{A} = \sqrt{A}\langle n|N\rangle = \langle n|\hat{N}\rangle. \quad (159)$$

Let’s compute  $A$  to second order in  $V$ :

$$\frac{1}{A} = \langle N|N\rangle \quad (160)$$

$$= \left( \langle n| + \lambda\langle N_1| + \lambda^2\langle N_2| \right) \left( |n\rangle + \lambda|N_1\rangle + \lambda^2|N_2\rangle \right) + O(\lambda^3) \quad (161)$$

$$= 1 + \lambda^2\langle N_1|N_1\rangle + O(\lambda^3) \quad (162)$$

$$= 1 + \lambda^2 \sum_{m \neq n} \langle N_1|m\rangle \langle m|N_1\rangle + O(\lambda^3) \quad (163)$$

$$= 1 + \lambda^2 \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{(\varepsilon_n - \varepsilon_m)^2} + \dots \quad (164)$$

We see that  $|N\rangle$  is normalized already to one to first order, with corrections only appearing at second order.

To second order,

$$\begin{aligned} A &= 1 - \lambda^2 \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{(\varepsilon_n - \varepsilon_m)^2} + O(\lambda^3) \\ &= \frac{\partial}{\partial \varepsilon_n} \left( \varepsilon_n + \lambda\langle n|V|n\rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{\varepsilon_n - \varepsilon_m} \right) + O(\lambda^3) \\ &= \frac{\partial E_n}{\partial \varepsilon_n} + O(\lambda^3). \end{aligned} \quad (165)$$

This result is actually valid to all orders in perturbation theory: If a system is in eigenstate  $|\hat{N}\rangle = \sqrt{A}|N\rangle$  of the perturbed Hamiltonian, the probability,  $A = |\langle n|\hat{N}\rangle|^2$ , to observe it in the unperturbed state,  $|n\rangle$ , is just the partial derivative,  $\partial E_n/\partial \varepsilon_n$ , of the perturbed energy with respect to the unperturbed energy. The partial derivative here means keeping  $\varepsilon_m$  ( $m \neq n$ ) and  $\langle m|V|n\rangle$  fixed.



## 6 Degenerate State Perturbation Theory

If  $\varepsilon_n = \varepsilon_m$  and  $\langle n|V|M\rangle \neq 0$ , then the perturbation theory we developed above breaks down. This is not an essential difficulty, however, and we address getting around it here.

Suppose that a set of states,

$$|n_1\rangle, |n_2\rangle, \dots, |n_\ell\rangle, \quad (166)$$

are degenerate with respect to  $H_0$ :

$$H_0|n_i\rangle = \varepsilon_n|n_i\rangle, \quad i = 1, 2, \dots, \ell. \quad (167)$$

As we already noticed, if  $\langle n_i|V|n_j\rangle \neq 0$  for  $i \neq j$ , the perturbation theory we have developed breaks down. However, we may choose any linear combinations of these degenerate states and again obtain eigenstates of  $H_0$  with the same eigenvalue. Thus, choose the set which diagonalizes  $V$  in this subspace:

$$|n'_i\rangle = \sum_{j=1}^{\ell} b_{ij}|n_j\rangle, \quad (168)$$

such that

$$\langle n'_i|V|n'_j\rangle = 0, \quad i \neq j \quad (169)$$

The matrix  $B = \{b_{ij}\}$  which does this is just the matrix formed by the normalized eigenvectors of the  $V$  matrix (in this  $\ell$ -dimensional subspace):

$$V\mathbf{B}_j = \lambda_j\mathbf{B}_j, \quad (170)$$

where

$$\sum_{i=1}^{\ell} |(\mathbf{B}_j)_i|^2 = 1. \quad (171)$$

Thus,

$$|n'_i\rangle = \sum_{j=1}^{\ell} (\mathbf{B}_i)_j |n_j\rangle. \quad (172)$$

With this change in basis, we recover our original first order perturbation theory result for the wave functions:

$$|N'_i\rangle = |n'_i\rangle + \sum_{m \notin \{n_k\}} \frac{|m\rangle \langle m|V|n'_i\rangle}{\varepsilon_n - \varepsilon_m} + \dots \quad (173)$$

We also recover our original second order perturbation theory result for the energies:

$$E_{n_i} = \varepsilon_n + \langle n'_i | V | n'_i \rangle + \sum_{m \notin \{n_k\}} \frac{|\langle m | V | n'_i \rangle|^2}{\varepsilon_n - \varepsilon_m} + \dots \quad (174)$$

## 7 Time-dependent Perturbation Theory

We now add an element of time variation to our discussion of perturbations. We'll develop the basic ideas here; they are especially useful in the application to scattering theory, which we'll treat at more length in a later note.

Suppose that, at some time  $t < t_0$ , the system is in a state  $|\psi_t^0\rangle$ , satisfying the Schrödinger equation:

$$i\partial_t |\psi_t^0\rangle = H_0 |\psi_t^0\rangle, \quad t < t_0. \quad (175)$$

At time  $t = t_0$ , we turn on a perturbing potential,  $V_t$ . For  $t > t_0$ , we thus must solve:

$$i\partial_t |\psi_t\rangle = (H_0 + V_t) |\psi_t\rangle, \quad t > t_0, \quad (176)$$

with the boundary condition

$$|\psi_t\rangle = |\psi_t^0\rangle, \quad t \leq t_0. \quad (177)$$

Often,  $V_t$  is “small enough” so that we can find an approximate solution, even if an exact solution is too daunting a prospect. As for the stationary state perturbation theory, we make an expansion in powers of  $V_t$ . Note that  $|\psi_t\rangle$  contains the time dependence from  $H_0$ , and if  $H_0 \gg V_t$ , we expect this to be a large portion of the time dependence. As this isn't usually the time dependence of interest in such problems, it is convenient to factor it out by writing:

$$|\psi_t\rangle = e^{-iH_0 t} |\psi(t)\rangle. \quad (178)$$

Then,

$$i\partial_t |\psi_t\rangle = H_0 |\psi_t\rangle + e^{-iH_0 t} i\partial_t |\psi(t)\rangle, \quad (179)$$

and hence:

$$e^{-iH_0 t} i\partial_t |\psi(t)\rangle = (i\partial_t - H_0) |\psi_t\rangle \quad (180)$$

$$= V_t |\psi_t\rangle \quad (181)$$

$$= V_t e^{-iH_0 t} |\psi(t)\rangle. \quad (182)$$

If we define

$$V(t) \equiv e^{iH_0 t} V_t e^{-iH_0 t}, \quad (183)$$

we may write

$$i\partial_t |\psi(t)\rangle = V(t) |\psi(t)\rangle. \quad (184)$$

We see that  $V(t)$  looks like a Hamiltonian for “state”  $|\psi(t)\rangle$ . We call  $|\psi(t)\rangle$  the state vector in the **interaction representation**, implying that the time dependence is due only to the interaction. The operator  $V(t)$  is the interaction representation for operator  $V_t$ . We may note that, if  $V_t = 0$ , the interaction representation is just the Heisenberg representation.

Now integrate with respect to time:

$$\int_{t_0}^t \partial_t |\psi(t)\rangle dt = |\psi(t)\rangle - |\psi(t_0)\rangle, \quad (185)$$

or,

$$|\psi(t)\rangle = |\psi(t_0)\rangle + \frac{1}{i} \int_{t_0}^t V(t_1) |\psi(t_1)\rangle dt_1. \quad (186)$$

This suggests that we try an iterative solution, which we hope converges. Thus, to first order in  $V$ :

$$|\psi(t)\rangle = |\psi(t_0)\rangle + \frac{1}{i} \int_{t_0}^t V(t_1) |\psi(t_0)\rangle dt_1. \quad (187)$$

To find the second order solution, we substitute the approximation of Eqn. 187 into Eqn. 186:

$$|\psi(t)\rangle = |\psi(t_0)\rangle + \frac{1}{i} \int_{t_0}^t dt_1 V(t_1) |\psi(t_0)\rangle + \left(\frac{1}{i}\right)^2 \int_{t_0}^t dt_1 V(t_1) \int_{t_0}^{t_1} dt_2 V(t_2) |\psi(t_0)\rangle. \quad (188)$$

In general, we see that the  $n$ th order correction in this expansion is:

$$\left(\frac{1}{i}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n V(t_1) V(t_2) \dots V(t_n) |\psi(t_0)\rangle. \quad (189)$$

If we define a kernel as  $K(t', t) = V(t)\theta(t' - t)$ , we see that this series is really in the form of a Neumann series for the solution of an integral equation.

## 7.1 The Time-Ordered Product

There is another interesting way to express this series result. Let us define the concept of a **time-ordered product**, denoted by  $\{AB\}_t$ , of two operators  $A$  and  $B$ , according to:

$$\{A(t_1)B(t_2)\}_t = \begin{cases} A(t_1)B(t_2), & \text{if } t_1 \geq t_2, \\ B(t_2)A(t_1) & \text{if } t_1 < t_2. \end{cases} \quad (190)$$

With this idea, consider

$$\left\{ \left[ \int_{t_0}^t V(t_1) dt_1 \right]^2 \right\}_t = \left\{ \int_{t_0}^t dt_1 V(t_1) \int_{t_0}^t dt_2 V(t_2) \right\}_t \quad (191)$$

$$= \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \{V(t_1)V(t_2)\}_t \quad (192)$$

$$= \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \{V(t_1)V(t_2)\}_t + \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \{V(t_2)V(t_1)\}_t \\ = 2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \{V(t_1)V(t_2)\}_t. \quad (193)$$

In general, we find:

$$\left\{ \left[ \int_{t_0}^t V(t_1) dt_1 \right]^n \right\}_t = \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \dots \int_{t_0}^t dt_n \{V(t_1)V(t_2)\dots V(t_n)\}_t \\ = n! \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n V(t_1)V(t_2)\dots V(t_n). \quad (194)$$

Thus,

$$\frac{1}{i^n n!} \left\{ \left[ \int_{t_0}^t V(t_1) dt_1 \right]^n \right\}_t |\psi(t_0)\rangle \quad (195)$$

is the  $n$ th order term in our expansion for  $|\psi(t)\rangle$ . We might think of this in terms of the picture in Fig. 3: Imagine that, in propagating from time  $t_0$  to time  $t$ , the wave “interacts” with the potential at discrete times  $t_1, t_2, \dots, t_n$ . To get the total evolution of the wave, we must integrate over all possible interaction times, and sum over all possible numbers of interactions. When we sum over all terms in this expansion, we find:

$$|\psi(t)\rangle = \left\{ \exp \left[ -i \int_{t_0}^t V(t_1) dt_1 \right] \right\}_t |\psi(t_0)\rangle. \quad (196)$$

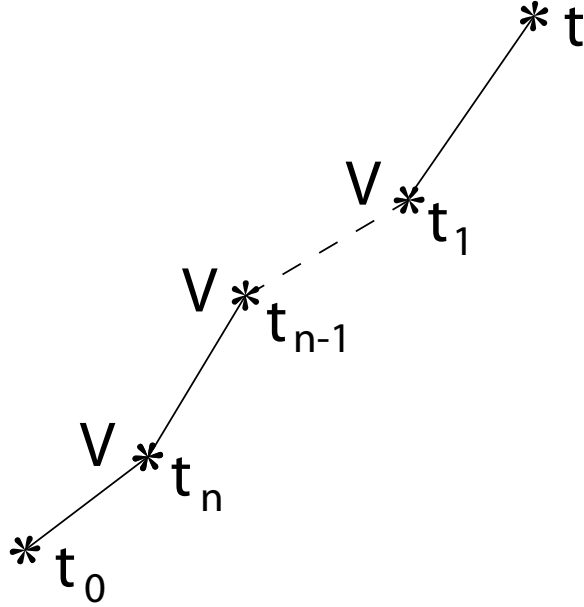


Figure 3: Illustration of  $n$ th order interaction term in time evolution from  $t_0$  to  $t$ .

## 7.2 Transition Probability, Fermi's Golden Rule

Suppose a system is initially (at  $t = t_0$ ) in eigenstate  $|i\rangle$  of  $H_0$ :

$$|\psi(t)\rangle = |i\rangle, \quad \text{where } H_0|i\rangle = \varepsilon_i|i\rangle. \quad (197)$$

Let  $|f\rangle$  denote an arbitrary eigenstate of  $H_0$ . For convenience, we choose  $|i\rangle$ ,  $|f\rangle$  to be in the interaction representation.

We wish to address the question: At time  $t > t_0$ , what is the probability that the system will be observed in state  $|f\rangle$ , *i.e.*, what is the probability that the interaction has caused the transition  $|i\rangle \rightarrow |f\rangle$ ? In the interaction representation, this amplitude is  $\langle f|\psi(t)\rangle$ . Using Eqn. 187, we have to first order in  $V$ :

$$\langle f|\psi(t)\rangle = \langle f|i\rangle + \frac{1}{i} \int_{t_0}^t dt_1 \langle f|V(t_1)|i\rangle. \quad (198)$$

We find for the matrix element in the integrand:

$$\langle f|V(t_1)|i\rangle = \langle f|e^{iH_0t_1}V_{t_1}e^{-iH_0t_1}|i\rangle \quad (199)$$

$$= e^{i(\varepsilon_f - \varepsilon_i)t_1} \langle f|V_{t_1}|i\rangle. \quad (200)$$

Hence, if  $\langle f|i\rangle = 0$ , the transition amplitude is

$$\langle f|\psi(t)\rangle = \frac{1}{i} \int_{t_0}^t dt_1 e^{i(\varepsilon_f - \varepsilon_i)t_1} \langle f|V_{t_1}|i\rangle. \quad (201)$$

The transition probability is:

$$P_{i \rightarrow f}(t) = |\langle f|\psi(t)\rangle|^2 = \left| \int_{t_0}^t dt_1 e^{i(\varepsilon_f - \varepsilon_i)t_1} \langle f|V_{t_1}|i\rangle \right|^2. \quad (202)$$

For example, suppose the potential is “turned on” at time  $t = 0$ , and is constant thereafter:

$$V_t = \begin{cases} 0, & t < t_0 = 0, \\ V = V(\mathbf{x}), & t > 0. \end{cases} \quad (203)$$

In this case,

$$P_{i \rightarrow f}(t) = \left| \int_{t_0}^t dt_1 e^{i(\varepsilon_f - \varepsilon_i)t_1} \langle f|V|i\rangle \right|^2 \quad (204)$$

$$= \left[ \frac{\sin \frac{\varepsilon_f - \varepsilon_i}{2} t}{\frac{\varepsilon_f - \varepsilon_i}{2}} \right]^2 |\langle f|V|i\rangle|^2. \quad (205)$$

This probability is plotted as a function of the energy difference in Fig. 4. The zeros occur at  $\varepsilon_f = \varepsilon_i \pm \frac{2\pi n}{t}$ ,  $n = 1, 2, \dots$ . The magnitudes of the bumps decrease as  $1/(\varepsilon_f - \varepsilon_i)^2$ .

For very small times,

$$P_{i \rightarrow f}(t) \approx t^2 |\langle f|V|i\rangle|^2, \quad (206)$$

approximately independent of  $\varepsilon_f - \varepsilon_i$ , if  $|\langle f|V|i\rangle|^2$  is not very dependent. As  $t$  increases, the probability is largest for states with  $\varepsilon_f$  near  $\varepsilon_i$  – the height of the central bump varies approximately as  $t^2$ , and the width as  $\frac{1}{t}$ , yielding a total probability to be in the central bump that grows approximately as  $t$ . This may be thought of in terms of an “uncertainty relation”: If the perturbation turns on, or acts, in a very short time  $\Delta t$ , transitions may be induced in first order to a wide range of energy states,

$$\Delta\varepsilon \Delta t \gtrsim \frac{2\pi}{\Delta t} \Delta t = 2\pi. \quad (207)$$

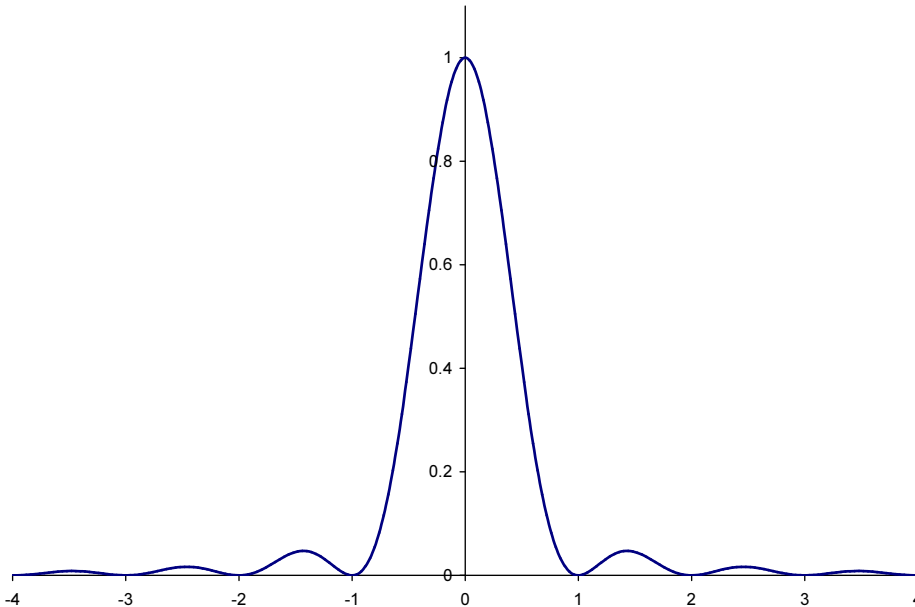


Figure 4: The  $i \rightarrow f$  transition probability as a function of energy difference. The vertical axis is  $P_{i \rightarrow f}(t)/|\langle f|V|i\rangle|^2$  in units of  $t^2$ . The horizontal axis is  $\varepsilon_f - \varepsilon_i$  in units of  $2\pi/t$ .

But as the interaction is turned on more slowly, or has acted for a longer time, the uncertainty in energy induced by the perturbation decreases, *i.e.*, energy is conserved to  $\Delta\varepsilon \sim 2\pi/t$ .

If the levels  $\varepsilon_f$  and  $\varepsilon_i$  are discrete, with  $\varepsilon_f \neq \varepsilon_i$ , the transition probability simply oscillates with period  $T = 2\pi/|\varepsilon_f - \varepsilon_i|$ . If  $|f\rangle$  and  $|i\rangle$  are degenerate, then the probability grows as  $t^2$ . This cannot continue indefinitely, since probabilities are bounded by one. Eventually, higher orders in the perturbation become important.

Consider the case where  $|f\rangle$  is drawn from a continuum of energy states (or, perhaps a very closely spaced spectrum). For example, we could be dealing with a free particle in  $H_0$ . In this case it makes more sense to ask for the transition probability to some set of states in a neighborhood of  $|n\rangle$ . For example, for a free particle, we are interested in the transition probability to phase space volume element  $d^3(\mathbf{p})$  about  $\mathbf{p}$ . Since the area of the central bump grows as  $t$ , we expect the transition probability to a set of such states

with  $\varepsilon_f \approx \varepsilon_i$  to grow linearly with time. Hence, the transition *rate* to such a set of states is a constant. Let us calculate the transition rate for this case.

We must sum Eqn. 205 over the region of interest (call this region  $R$ ):

$$\sum_{f \in R} P_{i \rightarrow f}(t) = \int_R d\varepsilon_f \rho(\varepsilon_f) \left[ \frac{\sin \frac{\varepsilon_f - \varepsilon_i}{2} t}{\frac{\varepsilon_f - \varepsilon_i}{2}} \right]^2 |\langle f|V|i \rangle|^2, \quad (208)$$

where  $\rho(\varepsilon_f)$  is the number of states per unit energy, known as the **density of states**. Let's suppose  $|\langle f|V|i \rangle|^2$  doesn't change much over the region of interest, and take this quantity outside the integration:

$$\sum_{f \in R} P_{i \rightarrow f}(t) \approx |\langle f|V|i \rangle|^2 \int_R d\varepsilon_f \rho(\varepsilon_f) \left[ \frac{\sin \frac{\varepsilon_f - \varepsilon_i}{2} t}{\frac{\varepsilon_f - \varepsilon_i}{2}} \right]^2, \quad (209)$$

As  $t$  becomes larger, the central bump falls entirely within  $R$ , and then the density of states can also be considered effectively constant over the sharply peaked integrand. Hence, we take  $\rho(\varepsilon_f)$  outside the integral also, in this limit:

$$\sum_{f \in R} P_{i \rightarrow f}(t) \approx [|\langle f|V|i \rangle|^2 \rho(\varepsilon_f)]_{\varepsilon_f = \varepsilon_i} \int_R d\varepsilon_f \left[ \frac{\sin \frac{\varepsilon_f - \varepsilon_i}{2} t}{\frac{\varepsilon_f - \varepsilon_i}{2}} \right]^2, \quad (210)$$

Finally, since the central peak is contained entirely within  $R$ , we may let the limits of integration go to  $\pm\infty$ .

We wish to evaluate the integral:

$$\int_{-\infty}^{\infty} d\varepsilon_f \left[ \frac{\sin \frac{\varepsilon_f - \varepsilon_i}{2} t}{\frac{\varepsilon_f - \varepsilon_i}{2}} \right]^2 = 2t \int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2}. \quad (211)$$

One way to compute this integral is to notice that

$$\sin^2 x = \frac{1}{2}(1 - \cos 2x) = \Re \frac{1 - e^{2ix}}{2}, \quad (212)$$

and consider the contour integral:

$$\frac{1}{2} \oint_C \frac{1 - e^{2iz}}{z^2} dz = 0 \quad (213)$$

around the contour in Fig. 5 The integral around the large semicircle is zero



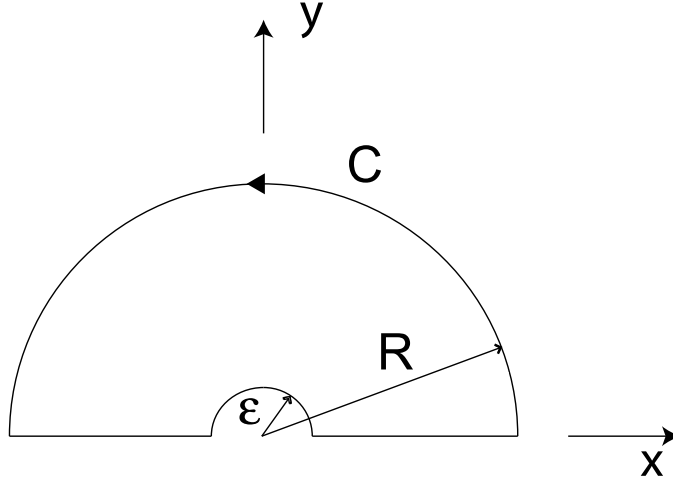


Figure 5: Contour for the evaluation of the integral in Eqn. 213.

in the limit  $R \rightarrow \infty$ . The desired integral is thus minus the integral around the small semicircle, in the limit  $\epsilon \rightarrow 0$ :

$$\int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} = -\lim_{\epsilon \rightarrow 0} \int_{\pi}^0 i\epsilon \frac{1 - e^{2i\epsilon e^{i\theta}}}{2\epsilon^2 e^{2i\theta}} d\theta \quad (214)$$

$$= -\frac{i}{2}(-2i) \int_{\pi}^0 d\theta \quad (215)$$

$$= \pi. \quad (216)$$

Hence,

$$\sum_{f \in R} P_{i \rightarrow f}(t) \approx \Gamma t, \quad (217)$$

where the transition rate,  $\Gamma$ , is:

$$\Gamma = 2\pi \left[ |\langle f | V | i \rangle|^2 \rho(\epsilon_f) \right]_{\epsilon_f = \epsilon_i}. \quad (218)$$

Equation 218 is an important result; it is known as **Fermi's Golden Rule**.

Our discussion is evidently not valid when:

1. The time  $t$  is too “short”. We must have the central bump within the region of interest. That is, we must have  $(\Delta\epsilon)_R$  large compared with

$2\pi/t$ , *i.e.*,

$$t > \frac{2\pi}{(\Delta\varepsilon)_R}. \quad (219)$$

2. The time  $t$  is too “long”. If  $t$  is too long, then there may be only a few states within the central bump (not a problem if the spectrum is continuous, of course). Suppose  $\delta\varepsilon$  is the level spacing in the region of interest. This spacing must be small compared with  $2\pi/t$  for the above analysis. That is, we must have

$$t \ll \frac{2\pi}{\delta\varepsilon}. \quad (220)$$

Furthermore, if  $t$  becomes too long, the initial state becomes depleted, and the transition rate will no longer be constant.

Let us apply this framework to the case of a particle in a box of volume  $L^3$ .<sup>2</sup> Turn on the potential  $V(x)$  inside the box. Start with a particle in momentum state  $\mathbf{p}$ , and ask for the rate at which it transitions to other momentum states,  $\mathbf{p}'$ . The matrix element of  $V(\mathbf{x})$  between momentum states is

$$\langle \mathbf{p}' | V | \mathbf{p} \rangle = \int_{L^3} d^3(\mathbf{x}) \frac{e^{-i\mathbf{p}'\cdot\mathbf{x}}}{L^{3/2}} V(\mathbf{x}) \frac{e^{i\mathbf{p}\cdot\mathbf{x}}}{L^{3/2}} \quad (221)$$

$$= \hat{V}(\mathbf{p}' - \mathbf{p}) / L^3, \quad (222)$$

where  $\hat{V}$  is the fourier transform (in the box) of  $V(\mathbf{x})$ .

To put this into the golden rule, we restate the golden rule somewhat: We notice that as  $t$  grows, the function

$$\left[ \frac{\sin \frac{\varepsilon_f - \varepsilon_i}{2} t}{\frac{\varepsilon_f - \varepsilon_i}{2}} \right]^2 \rightarrow_{t \rightarrow \infty} 2\pi t \delta(\varepsilon_f - \varepsilon_i). \quad (223)$$

Then our transition rate is:

$$\Gamma = 2\pi |\langle f | V | i \rangle|^2 \delta(\varepsilon_f - \varepsilon_i). \quad (224)$$

This version of Fermi’s Golden Rule must be applied in the context of a sum over states  $|f\rangle$ , that is, there must be an integral over the delta function.

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<sup>2</sup>We have in mind that we will eventually take the limit as the box size becomes infinite, and develop this into a theory for scattering.

Using Eqn. 224, the transition rate for  $\mathbf{p} \rightarrow \mathbf{p}'$  is:

$$\Gamma_{\mathbf{p} \rightarrow \mathbf{p}'} = 2\pi \frac{|\hat{V}(\mathbf{p}' - \mathbf{p})|^2}{L^6} \delta(\varepsilon_{\mathbf{p}'} - \varepsilon_{\mathbf{p}}), \quad (225)$$

where

$$\varepsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}. \quad (226)$$

The rate  $\Gamma$  here is actually a differential decay rate. Let us apply it to obtain the rate of scattering,  $d\Gamma$ , into an element of solid angle  $d\Omega'$ :

$$d\Gamma = \sum_{\mathbf{p}' \in d\Omega'} \Gamma_{\mathbf{p} \rightarrow \mathbf{p}'}. \quad (227)$$

To perform this summation, we need the density of states, *i.e.*, we need the number of states in phase space element  $d^3(\mathbf{p}')$ . On dimensional grounds, we must have a number of states  $dN'$ :

$$dN' \propto L^3 d^3(\mathbf{p}'), \quad (228)$$

and it remains to determine the constant of proportionality. Let's consider the problem in one dimension. The free particle wave functions are

$$\psi_p(x) = \frac{1}{\sqrt{L}} e^{\pm ipx}. \quad (229)$$

Imposing periodic boundary conditions ensures no net flux of particles out of the box<sup>3</sup>:

$$\psi(x) = \psi(x + L) \quad (230)$$

$$\psi'(x) = \psi'(x + L). \quad (231)$$

Thus, we must have  $e^{ipL} = 1$ , or  $pL = 2\pi n$ , where  $n$  is an integer. Hence,

$$\frac{dN}{dp} = \frac{L}{2\pi}. \quad (232)$$

We generalize to three dimensions to obtain

$$dN = \frac{L^3}{(2\pi)^3} d^3(\mathbf{p}). \quad (233)$$

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<sup>3</sup>Note that we are really thinking in terms of eventually letting the box boundaries go off to infinity, and the constraint we want is conservation of probability. We don't care here whether the wave function goes to zero at the box boundary.

Thus, we have

$$d\Gamma = \int_{\mathbf{p}' \in d\Omega'} \frac{L^3}{(2\pi)^3} d^3(\mathbf{p}') 2\pi \frac{|\hat{V}(\mathbf{p}' - \mathbf{p})|^2}{L^6} \delta(\varepsilon_{\mathbf{p}'} - \varepsilon_{\mathbf{p}}) \quad (234)$$

$$= \frac{d\Omega'}{L^3} \frac{m}{(2\pi)^2} \int_0^\infty p' d\varepsilon_{p'} |\hat{V}(\mathbf{p}' - \mathbf{p})|^2 \delta(\varepsilon_{p'} - \varepsilon_p) \quad (235)$$

$$= \frac{d\Omega'}{L^3} \frac{mp}{(2\pi)^2} |\hat{V}(\mathbf{p}' - \mathbf{p})|^2, \quad (236)$$

where  $\mathbf{p}' = |\mathbf{p}| \hat{\boldsymbol{\Omega}}'$ , with  $\hat{\boldsymbol{\Omega}}'$  a unit vector in  $d\Omega'$ .

We may think of this example as a “scattering experiment” since the potential is effectively “turned on” as the incident particle nears it. As long as the potential falls off rapidly enough at large distances, the use of free particle wave functions for the incident wave at early times and for the scattered wave at late times is a plausible approximation to make. If we suppose that we have a beam of incident particles, then Eqn. 236 tells us the rate at which particles scatter into  $d\Omega'$  per incident particle in volume  $L^3$ . The flux of particles per incident particle of momentum  $p$  in volume  $L^3$  is just:

$$\text{Number of beam/area/time} = \frac{1}{L^3} |\mathbf{v}| = \frac{p}{mL^3}. \quad (237)$$

This may be seen by interpreting the factor  $1/L^3$  as the number of beam particles per unit volume (*i.e.*, we have normalized our wave to one particle in the box of volume  $L^3$ ), and  $|\mathbf{v}|$  (the speed of a beam particle) gives the distance per unit time. Dividing the rate by this flux, we obtain the **differential scattering cross section**:

$$\frac{d\sigma}{d\Omega'} = \frac{m^2}{(2\pi)^2} |\hat{V}(\mathbf{p}' - \mathbf{p})|^2. \quad (238)$$

This formula is referred to as the **Born Approximation** (or, as the “first” Born approximation) for the differential cross section. Notice that the size of the box has disappeared once we have divided out the incident flux; we expect the formula to apply in the limit of infinite spatial extent (*i.e.*, in the continuum limit).

### 7.3 Coulomb Scattering

In Coulomb scattering, we consider the potential

$$V(\mathbf{x}) = \frac{q_1 q_2}{r}, \quad (239)$$

where  $r = |\mathbf{x}|$ . We need the Fourier transform:

$$\hat{V}(\mathbf{p}' - \mathbf{p})/q_1q_2 = \int_{(\infty)} d^3(\mathbf{x}) \frac{1}{r} e^{-i(\mathbf{p}' - \mathbf{p}) \cdot \mathbf{x}} \quad (240)$$

$$= 2\pi \int_0^\infty r dr \int_{-1}^1 d \cos \theta \exp(-i|\mathbf{p}' - \mathbf{p}|r \cos \theta) \quad (241)$$

$$= 2\pi \int_0^\infty r dr \frac{e^{-i|\mathbf{p}' - \mathbf{p}|r} - e^{i|\mathbf{p}' - \mathbf{p}|r}}{-i|\mathbf{p}' - \mathbf{p}|r} \quad (242)$$

$$= \frac{2\pi i}{(\mathbf{p}' - \mathbf{p})^2} (-2i) \int_0^\infty \sin x dx \quad (243)$$

$$= \frac{4\pi}{(\mathbf{p}' - \mathbf{p})^2}. \quad (244)$$

Actually, the integral  $\int_0^\infty \sin x dx = 1$  may be a bit suspicious. However, we get the same result if we consider scattering on a Yukawa potential and take the limit as the Yukawa range goes to infinity. Writing

$$(\mathbf{p}' - \mathbf{p})^2 = 2p^2(1 - \cos \theta), \quad (245)$$

we obtain the differential cross section:

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{4\pi^2} \frac{16\pi^2}{4p^4(1 - \cos \theta)^2} (q_1q_2)^2 \quad (246)$$

$$= \frac{(q_1q_2)^2 m^2}{p^4(1 - \cos \theta)^2} \quad (247)$$

$$= \frac{(q_1q_2)^2}{16E^2 \sin^4 \frac{\theta}{2}}, \quad (248)$$

where  $p^2 = 2mE$ , and  $\theta$  is the **scattering angle**. This result may be recognized as the Rutherford cross section. There should be some real concern whether we had any business applying the Born approximation here, since the Coulomb potential falls off so slowly with distance. We'll discuss this issue further later.

## 7.4 Decays

We are sometimes faced with the problem of describing a decay process, such as the radioactive decay of a nucleus, in which a particle of momentum  $\mathbf{p}$

is produced. To be more explicit, suppose that we have a nucleus in an initial state  $|i\rangle$  which decays to a final state  $|f\rangle$  plus a particle in momentum state  $|\mathbf{p}\rangle$ . We'll neglect the nuclear recoil here, *i.e.*, we'll assume that the momentum  $\mathbf{p}$  is small compared with the nuclear masses involved.

Assume that we know the interaction matrix element,  $\langle f; \mathbf{p} | V | i \rangle$  for the decay. The differential rate to emit the particle into solid angle element  $d\Omega$  is

$$d\Gamma = d\Omega \int_0^\infty \frac{mpL^3}{(2\pi)^3} d\varepsilon_p 2\pi |\langle f; \mathbf{p} | V | i \rangle|^2 \delta(E_i - E_f - \varepsilon_p) \quad (249)$$

$$= d\Omega \frac{mpL^3}{(2\pi)^2} |\langle f; \mathbf{p} | V | i \rangle|^2, \quad (250)$$

where we have used

$$dN = \frac{L^3}{(2\pi^3)} d^3(\mathbf{p}) = d\Omega \frac{L^3}{(2\pi)^3} p m d\varepsilon_p, \quad (251)$$

$E_i$  is the energy of the nucleus in the initial state,  $E_f$  is the energy of the nucleus in the final state,  $\varepsilon_p = p^2/2m$ ,  $\mathbf{p} = p\hat{\Omega}$ , and  $p = \sqrt{2m(E_i - E_f)}$ . Note that the wave function of the emitted particle will have a normalization proportional to  $1/L^{3/2}$ , so the rate will actually be independent of  $L$ .

Integrating over  $d\Omega$  gives the total decay rate:

$$\Gamma = \frac{mpL^3}{4\pi^2} \int_{(4\pi)} d\Omega |\langle f; \mathbf{p} | V | i \rangle|^2. \quad (252)$$

If at  $t = 0$  we have  $N_0$  nuclei in state  $|i\rangle$ , then at later time  $t$  we will have seen  $\Delta N = N_0 \Gamma t$  decays, according to first order perturbation theory. For large times, this must break down, since the initial state becomes depleted. We may rectify this by writing

$$\frac{dN}{dt} = -N(t)\Gamma, \quad (253)$$

*i.e.*, the rate of observing nuclear decays is proportional the number of available nuclei, as well as to the decay rate of a nucleus. Thus, we have the familiar exponential decay law:

$$N(t) = N_0 e^{-\Gamma t}. \quad (254)$$

## 7.5 Adiabatically Increasing Potential

Earlier, we considered that our potential was turned on more-or-less suddenly at some time  $t_0$ . Let us consider the situation where the potential is turned on very slowly, compared with some relevant time scale. We'll see that this case is not fundamentally different from our previous discussion, in the spirit of the perturbative nature of the interaction.

Let us consider a situation where we imagine a slow turn-on of a potential, for example, suppose we have an atom in state  $|i\rangle$  which we subject to an electromagnetic field which is slowly increased from zero. A measure of "slow" here must mean that the rate of energy change associated with the external field must be small compared with the orbit frequency of the atomic electrons, *i.e.*, the time scale for significant variation must be longer than

$$\sim \frac{a_0}{v} \sim \frac{1}{m\alpha} \frac{1}{\alpha} \sim 10^{-16} \text{ s.} \quad (255)$$

Formally, we may turn on a potential,  $V$ , slowly by writing

$$V_t = e^{\gamma t} V, \quad (256)$$

where  $\gamma > 0$  so that  $V_{-\infty} \rightarrow 0$ . We'll assume here that  $V$  itself is independent of time. To first order in time-dependent perturbation theory:

$$|\psi(t)\rangle = |\psi(t_0)\rangle + \frac{1}{i} \int_{t_0}^t dt_1 V(t_1) |\psi(t_0)\rangle. \quad (257)$$

Consider the transition from  $|i\rangle$  to  $|f\rangle$ , assuming  $|i\rangle$  and  $|f\rangle$  are orthogonal. The transition amplitude, in first order, is:

$$\langle f | \psi(t) \rangle = \frac{1}{i} \int_{t_0 \rightarrow -\infty}^t dt_1 \langle f | V(t_1) | i \rangle \quad (258)$$

$$= \frac{1}{i} \int_{-\infty}^t dt_1 \langle f | e^{iH_0 t_1} V_{t_1} e^{-iH_0 t_1} | i \rangle \quad (259)$$

$$= \frac{1}{i} \int_{-\infty}^t dt_1 e^{i(\varepsilon_f - \varepsilon_i)t_1} e^{\gamma t_1} \langle f | V | i \rangle \quad (260)$$

$$= \frac{e^{\gamma t + i(\varepsilon_f - \varepsilon_i)t}}{\varepsilon_i - \varepsilon_f + i\gamma} \langle f | V | i \rangle. \quad (261)$$

The resulting transition probability is:

$$|\langle f | \psi(t) \rangle|^2 = \frac{e^{2\gamma t}}{(\varepsilon_f - \varepsilon_i)^2 + \gamma^2} |\langle f | V | i \rangle|^2. \quad (262)$$

The dependence of this probability on energy is in the form of a **Breit-Wigner** distribution, or of a **Cauchy** probability distribution. The energy

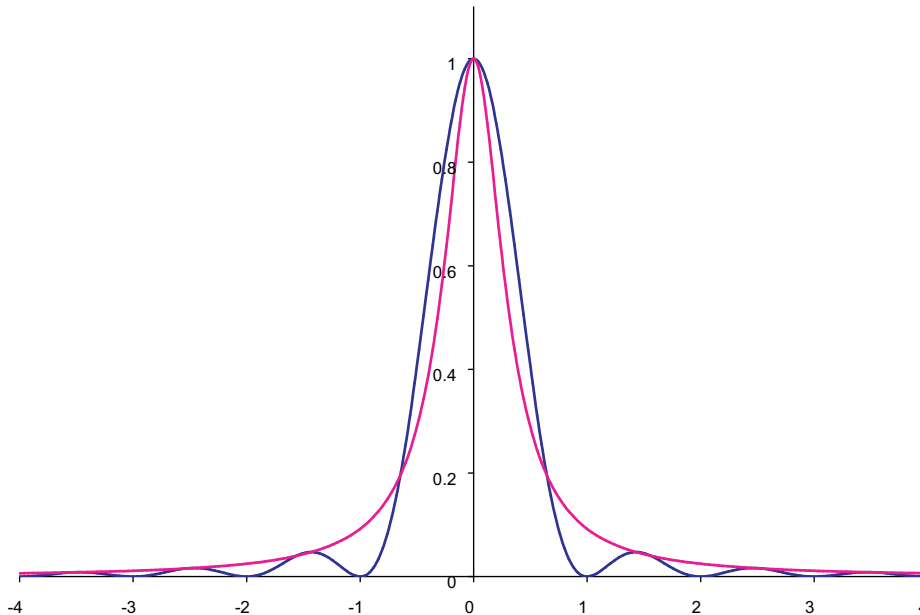


Figure 6: The  $i \rightarrow f$  transition probability as a function of energy difference. The smooth curve is  $\gamma^2/[(\varepsilon_f - \varepsilon_i)^2 + \gamma^2]$ , plotted for  $\gamma = 2$ . The horizontal axis is  $\varepsilon_f - \varepsilon_i$  in units of  $2\pi/t$ . The wavy curve is reproduced from Fig. 4 for comparison.

spread of this distribution is of order  $\gamma$ , which may be interpreted roughly as the inverse of the length of time the potential has been “on”.<sup>4</sup>

If  $|f\rangle$  is one of a continuum of states, we may calculate the transition rate to such states according to:

$$\frac{d}{dt} |\langle f | \psi(t) \rangle|^2 = e^{2\gamma t} \frac{2\gamma}{(\varepsilon_f - \varepsilon_i)^2 + \gamma^2} |\langle f | V | i \rangle|^2. \quad (263)$$

Consider the limit of arbitrarily slow turn-on:  $\gamma \rightarrow 0$ , and

$$\lim_{\gamma \rightarrow 0} e^{2\gamma t} \frac{2\gamma}{(\varepsilon_f - \varepsilon_i)^2 + \gamma^2} \rightarrow A\delta(\varepsilon_f - \varepsilon_i), \quad (264)$$

---

<sup>4</sup>Note that the standard deviation, or rms spread, of a Cauchy distribution is infinite. Hence, we use here something like the half width at half maximum as our measure of energy spread.



where  $A$  is a constant to be determined by matching the normalization in the  $\gamma \rightarrow 0$  limit:

$$A = \int_{-\infty}^{\infty} d\varepsilon_f \frac{2\gamma}{(\varepsilon_f - \varepsilon_i)^2 + \gamma^2} \quad (265)$$

$$= 2 \int_{-\infty}^{\infty} \frac{dx}{1+x^2} \quad (266)$$

$$= 2\pi. \quad (267)$$

Thus, we have the transition rate

$$\Gamma_{i \rightarrow f} = 2\pi |\langle f|V|i \rangle|^2 \delta(\varepsilon_f - \varepsilon_i), \quad (268)$$

which we recognize as Fermi's Golden rule once again! We observe that this rule is robust with respect to the details of how the perturbing potential is turned on.

## 8 Eigenvalues – Comparison Theorems

We return to some further discussion of some techniques similar to our discussion of the variational method. Consider the problem of a particle in a (time-independent) potential, and ask what we might say qualitatively about the existence and number of bound states, and related questions.

We start with the following “comparison theorem”:

**Theorem:** Consider a self-adjoint Hamiltonian:

$$H = -\frac{1}{2m} \nabla^2 + V(x). \quad (269)$$

Let  $\theta > 0$ . Then

$$H(\theta) = -\frac{1}{2m} \nabla^2 + \theta^2 V(\theta \mathbf{x}) \quad (270)$$

is also self-adjoint, and if  $\psi(\mathbf{x}) \in D_H$ , then  $\psi(\theta \mathbf{x}) \in D_{H(\theta)}$ . If  $\lambda$  is an eigenvalue of  $H$  ( $\lambda \in \Sigma(H)$ ), then  $\theta^2 \lambda$  is an eigenvalue of  $H(\theta)$ , and we have:

$$\Sigma[H(\theta)] = \{\theta^2 \lambda | \lambda \in \Sigma(H)\}. \quad (271)$$

In particular, if the negative spectrum of  $H$  is discrete (with only 0 as a possible point of accumulation), then the number of negative eigenvalues of  $H(\theta)$  is the same as of  $H$ .

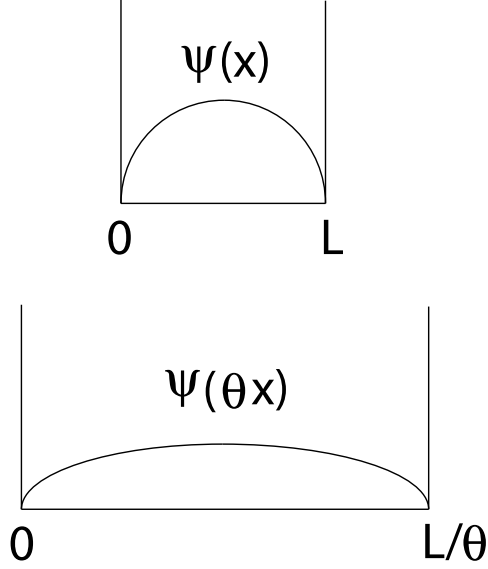


Figure 7: Illustration of the scaling of the wave function corresponding to the scaling of the potential.

**Proof:** Domain is a question of boundary conditions – the vectors must scale in the same way the potential is scaled. See Fig. 7 for an illustration.

Let  $H\psi(\mathbf{x}) = \lambda\psi(\mathbf{x})$ . Consider:

$$H(\theta)\psi(\theta\mathbf{x}) = \left[ -\frac{1}{2m}\partial_{\mathbf{x}}^2 + \theta^2V(\theta\mathbf{x}) \right] \psi(\theta\mathbf{x}) \quad (272)$$

$$= \theta^2 \left[ -\frac{1}{2m}\partial_{\theta\mathbf{x}}^2 + V(\theta\mathbf{x}) \right] \psi(\theta\mathbf{x}) \quad (273)$$

$$= \theta^2\lambda\psi(\theta\mathbf{x}). \quad (274)$$

This “comparison theorem”, relating the spectra of two related operators, tells us, for example, that any valid formula which gives an upper/lower limit on the number of negative eigenvalues in terms of the potential must be invariant under the substitution  $V(\mathbf{x}) \rightarrow \theta^2V(\theta\mathbf{x})$ , for  $\theta > 0$ . For example, consider

$$H = \frac{p^2}{2m} - V_0 + \frac{1}{2}kx^2. \quad (275)$$

The energy levels are at  $-V_0 + (n + 1/2)\omega$ , where  $\omega = \sqrt{k/m}$ . The number

of negative eigenvalues is  $n = \lfloor \frac{V_0}{\omega} - \frac{1}{2} \rfloor$ . Now consider modifying the potential from  $V(x) = -V_0 + \frac{1}{2}kx^2$  to

$$\theta^2 V(\theta x) = -\theta^2 V_0 + \theta^4 \frac{1}{2} k x^2, \quad (276)$$

giving the spectrum:

$$\Sigma[H(\theta)] = \left\{ \theta^2 \left[ -V_0 + \left( n + \frac{1}{2} \right) \right] \right\}. \quad (277)$$

The solution for the number of negative eigenvalues is the same as before.

Now consider, for a finite dimensional Hilbert space the following “min-max” theorem:

**Theorem:** Let  $Q$  be a Hermitian  $N \times N$  matrix, with eigenvalues:

$$\lambda_1 \leq \lambda_2 \leq \dots \leq \lambda_N. \quad (278)$$

Let  $P_k, 1 \leq k \leq N$  be the set of Hermitian projections onto a  $k$ -dimensional subspace. Then:

$$\lambda_n = \min_{F \in P_n} \left( \max_{\psi \in F, \|\psi\|=1} \langle \psi | Q | \psi \rangle \right), \quad (279)$$

where we use the symbol  $F$  to mean both the projection operator onto a subspace, and the corresponding subspace itself.

This theorem tells us that we can find the  $n$ th eigenvalue by first finding the maximum of  $\langle \psi | Q | \psi \rangle$  for all unit vectors  $\psi$  in a fixed  $n$ -dimensional subspace  $F$ , and then minimizing the result as a function of  $F$ . If we don't minimize, then we obtain an upper bound on  $\lambda_n$ . The case  $n = 1$  corresponds to the variational principle we have already discussed, since the subspaces are then one-dimensional, hence there is only one unit vector in each subspace (*i.e.*, there is no maximization step required), and our minimization step is only to the extent of our trial function parameterization. The case  $n = N$  is also trivial, since then  $F = \mathcal{H}$ , and there is thus no minimization step.

**Proof:** We have already dealt with the trivial cases  $n = 1$  and  $n = N$ , so we now suppose that  $1 < n < N$ . Since  $Q$  is Hermitian, it has the spectral decomposition:

$$Q = \sum_{k=1}^N \lambda_k E_k, \quad (280)$$

where  $E_k E_\ell = \delta_{k\ell}$  and  $I = \sum_{k=1}^N E_k$ . That is, the  $E_k$  are Hermitian projections into one-dimensional subspaces. Then we can write:

$$Q = \lambda_n I + \sum_{k=n}^N (\lambda_k - \lambda_n) E_k - \sum_{k=1}^n (\lambda_n - \lambda_k) E_k. \quad (281)$$

Hence, for any  $\|\psi\| = 1$ :

$$\langle \psi | Q | \psi \rangle = \lambda_n + \left| \sum_{k=n}^N (\lambda_k - \lambda_n) E_k \right| - \left| \sum_{k=1}^n (\lambda_n - \lambda_k) E_k \right|, \quad (282)$$

where taking the absolute values does not alter the validity, since each term in the two sums is non-negative. Now let  $F$  be any  $n$ -dimensional subspace, and let  $\psi \in F$ . Select  $\psi$  to be orthogonal to  $E_1, E_2, \dots, E_{n-1}$ , that is, orthogonal to these  $n-1$  projections. This is certainly possible, since there are  $n$  independent directions in  $F$ . Then we have:

$$\langle \psi | Q | \psi \rangle = \lambda_n + \left| \sum_{k=n}^N (\lambda_k - \lambda_n) E_k \right| \quad (283)$$

$$\geq \lambda_n. \quad (284)$$

Now select  $F$  orthogonal to  $E_{n+1}, E_{n+2}, \dots, E_N$ . Again, this is certainly possible, since there are still  $n$  directions left. In this case,

$$\langle \psi | Q | \psi \rangle = \lambda_n - \left| \sum_{k=1}^n (\lambda_n - \lambda_k) E_k \right| \quad (285)$$

$$\leq \lambda_n. \quad (286)$$

For both statements 284 and 286 to be true, we must have the statement in the theorem.

From the minmax theorem, it follows that:

**Theorem:** Let  $Q$  and  $V$  be  $N \times N$  Hermitian matrices, and let:

$$\hat{Q} \equiv Q + V. \quad (287)$$

Also, let the spectra of these operators be denoted:

$$\Sigma(Q) = \{\lambda_1 \leq \lambda_2 \leq \dots \leq \lambda_N\}, \quad (288)$$

$$\Sigma(\hat{Q}) = \{\hat{\lambda}_1 \leq \hat{\lambda}_2 \leq \dots \leq \hat{\lambda}_N\}, \quad (289)$$

$$\Sigma(V) = \{V_1 \leq V_2 \leq \dots \leq V_N\}. \quad (290)$$

Then

$$\lambda_n + V_N \geq \hat{\lambda}_n \geq \lambda_n + V_1. \quad (291)$$

It also follows that:

**Theorem:** Let  $Q$  be an  $N \times N$  Hermitian matrix with spectrum

$$\Sigma(Q) = \{\lambda_1 \leq \lambda_2 \leq \dots \leq \lambda_N\}. \quad (292)$$

Let  $P_k$  be any  $k$ -dimensional Hermitian projection,  $1 \leq k \leq N$ . We may regard the operator  $P_k Q P_k$  as a Hermitian  $k \times k$  matrix, when restricted to the subspace  $P_k$ . Let the eigenvalues of this restricted matrix be

$$\{\hat{\lambda}_1 \leq \hat{\lambda}_2 \leq \dots \leq \hat{\lambda}_k\}. \quad (293)$$

Then

$$\hat{\lambda}_n \geq \lambda_n, \text{ for } n = 1, 2, \dots, k. \quad (294)$$

We may see a classical analog of these theorems in terms of a system of coupled oscillators: First, if we add more springs to a system, none of the normal-mode frequencies decrease. Second, if we remove degrees of freedom by clamping, then the  $k$  remaining frequencies will be at least as large as the  $k$  lowest frequencies of the original unclamped system.

## 9 Exercises

1. Prove the theorem quoted in section 2.3:

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

$$E_0 \leq \langle \psi | H | \psi \rangle \leq E_1, \quad (295)$$

then

$$E_0 \geq \langle \psi | H | \psi \rangle - \frac{\langle H \psi | H \psi \rangle - \langle \psi | H | \psi \rangle^2}{E_1 - \langle \psi | H | \psi \rangle}. \quad (296)$$

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:

$$H(Z, N) = H_{\text{kin}} - ZV_c + V_e \quad (297)$$

$$H_{\text{kin}} = \sum_{n=1}^N \frac{\mathbf{p}_n^2}{2m}, \quad (298)$$

$$\text{where} \quad (299)$$

$$V_c = \alpha \sum_{n=1}^N \frac{1}{|\mathbf{x}_n|} \quad (300)$$

$$V_e = \alpha \sum_{N \geq j > k \geq 1} \frac{1}{|\mathbf{x}_k - \mathbf{x}_j|} \quad (301)$$

$$m = \text{electron mass} \quad (302)$$

$$\alpha = \text{fine structure constant.} \quad (303)$$

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).
- (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:

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

- (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?

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

$$V(r) = -G \frac{Mm}{r} \quad (304)$$

$$= -G \frac{Mm}{R+z} \quad (305)$$

$$\approx -G \frac{Mm}{R} + mgz \quad (306)$$

where (307)

$$M = \text{mass of earth} \quad (308)$$

$$m = \text{mass of particle} \quad (309)$$

$$r = \text{distance from center of earth} \quad (310)$$

$$G = \text{Newton's gravitational constant} \quad (311)$$

$$R = \text{radius of earth} \quad (312)$$

$$z = \text{height of particle above surface of earth} \quad (313)$$

$$g = GM/R^2. \quad (314)$$

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

$$I(\epsilon) = \int_{-\infty}^{\infty} f(x) e^{i\theta(x)/\epsilon} dx, \quad (315)$$

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

$$I(\epsilon) = \sqrt{\epsilon} f(x_0) e^{i\theta(x_0)/\epsilon} e^{i\frac{\pi}{4} \text{sign}[\theta''(x_0)]} \sqrt{\frac{2\pi}{|\theta''(x_0)|}} [1 + O(\epsilon)]. \quad (316)$$

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  $t$ :

$$J(t) = \int_0^1 \cos [t(x^3 - x)] dx. \quad (317)$$

5. I suggested in section 4.3 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:

$$V(x) = \begin{cases} -K & x \in (-\Delta/2, \Delta/2) \\ 0 & \text{otherwise.} \end{cases} \quad (318)$$

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:

$$\hat{\psi}(p) = \left[ \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{p-q}{\sigma}\right)^2} \right]^{1/2}. \quad (319)$$

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.

- (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.

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:  $\mathbf{E} = E\hat{\mathbf{e}}_z$ . 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  $L_z$ .
- (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?
- (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.
- (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?

8. It may happen that we encounter a situation where the eigenvalues of  $H_0$ , call them  $\varepsilon_n$  and  $\varepsilon_m$ , 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

$$V = \sum_{i,j} |i\rangle \langle i| V |j\rangle \langle j| \quad (320)$$

$$H_0 |i\rangle = \varepsilon_i |i\rangle, \quad (321)$$

where

$$\langle i|j\rangle = \delta_{ij}. \quad (322)$$

Let

$$V = V_1 + V_2, \quad (323)$$

with

$$V_1 \equiv |m\rangle \langle m| V |m\rangle \langle m| + |n\rangle \langle n| V |n\rangle \langle n| + \quad (324)$$

$$+ |m\rangle \langle m| V |n\rangle \langle n| + |n\rangle \langle n| V |m\rangle \langle m| \quad (325)$$

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.)

- (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  $|p\rangle = \frac{1}{\sqrt{L}}e^{2\pi in_p x/L}$ , determine all nonvanishing matrix elements of  $V$  :

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

Express your answer in terms of  $V_n$ .

- (c) Suppose  $\varepsilon_{n_p}$  and  $\varepsilon_{n_q}$  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.
- (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  $H_0$ ?
- (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. 8 for higher values of  $|p|$ .
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

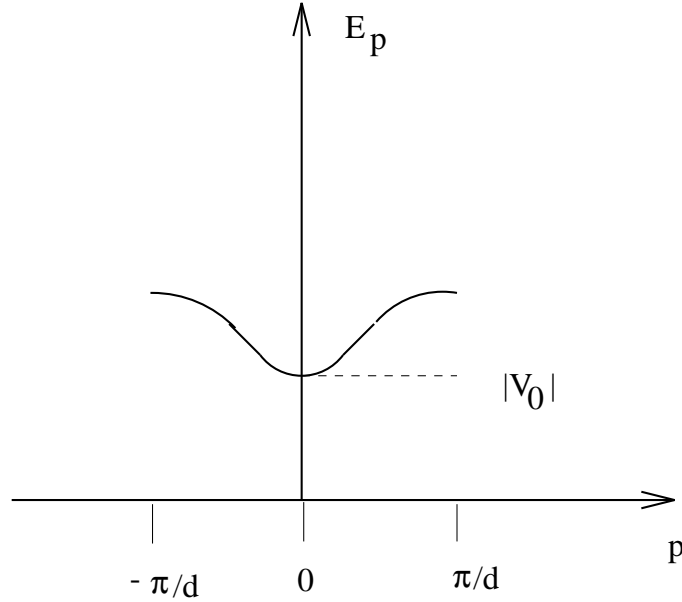


Figure 8: Energy versus momentum for the one-dimensional lattice problem (6).

$-L/2$  to  $L/2$ . Remembering that the Hilbert space of allowed states is a linear space, show that the periodic boundary condition:

$$\psi(-L/2) = \psi(L/2), \quad (326)$$

$$\psi'(-L/2) = \psi'(L/2) \quad (327)$$

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?

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

$$\frac{d\sigma}{d\Omega'} = \frac{m^2}{(2\pi)^2} |\hat{V}(\mathbf{p}' - \mathbf{p})|^2. \quad (328)$$

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

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.  $\mu$  itself has units of mass – note that as  $\mu \rightarrow 0$  we obtain the Coulomb potential:  $\mu$  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  $\mu$  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.
- (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.
- (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?