

Approximation Methods in Quantum Mechanics
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1 Roll-call of some approximation methods in quantum mechanics

For most interesting quantum mechanical systems (such as a many-electron atom) we do not know how to solve the time-dependent Schrodinger equation or the Schrödinger eigenvalue problem for stationary states and energy levels. There are exceptional 'exactly-solved' systems such as the free particle, square well, 1 dimensional Dirac delta, harmonic oscillator and sech^2 potentials, rigid body with an axis of symmetry, hydrogen atom, charged particle on a plane in an orthogonal constant magnetic field, spin in a magnetic field, Matthews-Lakshmanan oscillator

etc. For other systems (E.g. Helium atom, anharmonic oscillator, Hydrogen atom in an electric or magnetic field, atom exposed to EM radiation, relativistic and spin-orbit effects in Hydrogen, anisotropic molecule, many electron atoms, molecules etc.) we rely on various approximation methods. Sometimes, even ‘exactly-solvable’ systems are treated using approximation methods since they may be simpler and adequate! Some approximation methods are listed below:

- Variational approximations from the (Rayleigh-Ritz) variational principle
- Time-independent perturbation theory for Schrödinger eigenvalue problem
- Time-dependent perturbation theory and Fermi’s golden rule
- Semiclassical approximation and the WKB method.
- Bohr-Sommerfeld approximation for excited states
- Partial wave approximation in potential scattering.
- Born’s series and approximation in scattering theory
- Adiabatic approximation and geometric phase
- Hartree-Fock and Thomas-Fermi approximations for many electron atoms.
- Mean field and Density functional approximations in many-body quantum theory.
- Numerical approximation methods.

In these lectures, we will discuss only the rudiments of variational, perturbative, semi-classical and Born’s approximations.

2 Variational Principle and Approximations

- Suppose we have a particle moving in a potential V with Hamiltonian $H = T + V$ where $T = -(\hbar^2/2m)\nabla^2$. Assuming the spectrum of energies is bounded below, to begin with, we want to find the ground state, the eigenstate of H with lowest energy eigenvalue. Interestingly, there is an alternate characterization of the ground state among all normalizable states (not just among all eigenstates). It is the one which minimizes the expectation value $\langle H \rangle_\psi = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$ among all normalizable states. More generally, the energy eigenstates are precisely the extrema of $\langle H \rangle_\psi$. This is the statement of the Rayleigh-Ritz (RR) variational principle.

- Let us see why the RR variational principle is equivalent to the Schrodinger eigenvalue problem. To extremize the expectation value $\langle H \rangle_\psi$ among all normalizable states is the same as extremizing $\langle \psi | H | \psi \rangle$ among all unit norm states. We have the classic problem of extremizing a function ($F = \langle \psi | H | \psi \rangle$) subject to a constraint. Here the constraint is $C = \langle \psi | \psi \rangle - 1 = 0$. The method of Lagrange multipliers says that to extremize F subject to the constraint C is the same as extremizing $F - \lambda C$ where λ is a number called the Lagrange multiplier. λ is not known in advance, there are typically several allowed values of λ corresponding to several extrema of F subject to the constraint C . The physical meaning of λ in the RR principle will be clarified shortly.

- The condition for extrema is $\nabla F = \lambda \nabla C$. Geometrically this says that ∇F must point along/opposite to ∇C . Since ∇C points normal to the constraint ‘surface’ this would ensure ∇F is also normal to the constraint surface. In other words F , would be stationary on the constraint surface.

- Applying the method of Lagrange multipliers to the RR variational principle, we must extremize

$$\langle \psi | H | \psi \rangle - \lambda (\langle \psi | \psi \rangle - 1) \quad \text{or} \quad \int \psi^* H \psi d^3r - \lambda \left(\int \psi^* \psi d^3r - 1 \right). \quad (1)$$

Taking the variational derivative with respect to ψ^* we get $H\psi - \lambda\psi = 0$. We recognise this as the time-independent Schrodinger eigenvalue problem, with λ the energy eigenvalue. We should expect there to be several extrema corresponding to the various energy levels of the system.

2.1 Ground state variational principle for simple harmonic oscillator (SHO)

- Let us consider the 1D SHO with $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 x^2$. We wish to apply the variational principle to the problem of finding the g.s. energy and wavefunction of the SHO. For those not familiar with variational derivatives, we give another way of obtaining the above RR ground state variational principle.

- We first notice that the kinetic energy expectation value may be rewritten in a manifestly positive form after an integration by parts assuming $\psi(x) \rightarrow 0$ as $|x| \rightarrow \infty$

$$\langle T \rangle = -\frac{\hbar^2}{2m \|\psi\|^2} \int \psi^* \psi'' dx = \frac{\hbar^2}{2m \|\psi\|^2} \int \psi'(x)^* \psi'(x) dx = \frac{\hbar^2}{2m \|\psi\|^2} \int |\psi'(x)|^2 dx \geq 0. \quad (2)$$

$V(x) = \frac{1}{2} m \omega^2 x^2$ is also non-negative, so the expectation value of energy in any state is ≥ 0

$$E(\psi) = \frac{1}{\langle \psi | \psi \rangle} \left[\int \left(\frac{\hbar^2}{2m} |\psi'(x)|^2 + \frac{1}{2} m \omega^2 x^2 |\psi(x)|^2 \right) dx \right] \geq 0. \quad (3)$$

The energy eigenvalues are just expectation values of the Hamiltonian in the eigenstates. So it follows that the energy levels E_n (assumed discrete for convenience, it can be shown that the SHO spectrum is indeed discrete) must also be positive. So let us order them as $0 \leq E_0 < E_1 < E_2 < \dots$.

- Given any unit-norm state ψ we can expand it in the orthonormal energy eigenstates $|\psi_n\rangle = \sum_n c_n |\psi_n\rangle$ and write

$$\langle H \rangle_\psi = \sum_n |c_n|^2 E_n, \quad \text{where} \quad \sum_n |c_n|^2 = 1. \quad (4)$$

To minimize $\langle H \rangle$, we must select $|c_0|^2 = 1$ and $|c_{n>0}|^2 = 0$ ¹. In other words, the state with the least energy eigenvalue (g.s.) is the one which minimizes $\langle H \rangle_\psi$!

$$E_0 = \min_{\|\psi\|=1} \langle \psi | H | \psi \rangle \quad (5)$$

¹Though it may seem reasonable, we have not *proved* that the choice $|c_n|^2 = \delta_{n,0}$ minimizes $\langle H \rangle$. This is a problem in linear programming. Let $s_n = |c_n|^2$, then $\langle H \rangle = \sum_n s_n E_n$ with $\sum_n s_n = 1$. So $\langle H \rangle$ is a linear function of the variables s_n with non-negative coefficients, subject to the constraints $0 \leq s_n \leq 1$ and $\sum_n s_n = 1$. From linear programming, the minimum of $\langle H \rangle$ must occur at a boundary point of the region of allowed values of s_n . By repeated use of this fact one can show that $\langle H \rangle$ is minimal when $s_0 = 1$ and $s_{n \geq 1} = 0$. For example, if there are only two energy levels, $\langle H \rangle = s_0 E_0 + (1 - s_0) E_1$ is a linear function and is clearly minimal at $s_0 = 1$. More generally, $\frac{\partial \langle H \rangle}{\partial s_n} = E_n \geq 0$ with the slopes growing with n . So to minimize $\langle H \rangle$ we must choose the s_n as small as possible subject to the constraints and this is the above boundary point.

2.2 Variational approximation for SHO ground state

Suppose we want to find the g.s. approximately. It is usually too hard to minimize $\langle H \rangle_\psi$ over all square integrable $\psi(x)$. By minimizing it over a restricted class of wave functions, we will get an upper bound for the ground state energy and the best approximation to the g.s. wave function from that restricted class.

- Let us get a variational estimate for the gs energy and wave function of the harmonic oscillator by taking a unit norm gaussian variational ansatz/guess (use $I = \int e^{-\alpha x^2} = \sqrt{\pi/\alpha}$)

$$\psi_a(x) = Ae^{-x^2/4a^2}, \quad A = \frac{1}{\sqrt{a}(2\pi)^{1/4}}, \quad a > 0 \quad (6)$$

A gaussian is reasonable since we are looking for bound states and we expect the probability of finding the particle far from the point of equilibrium to be very small. The width of the gaussian is our variational parameter. We want to find the width 'a' for which $\langle H \rangle$ is minimal. If a is large, the potential energy will be large and if a is small, the derivative of ψ will induce a large kinetic energy. So we expect an optimal intermediate value of a for which the energy is minimal.

- Notice that our variational ansatz for the g.s. has no nodes (zeros at finite values of x). This is also a feature of the g.s. of a particle in a square well. If a wave function has many nodes, it must oscillate and have a large kinetic energy and would not minimize the energy.

- $V(x)$ is real, so the eigenstates can be taken real, that's why we picked a real $\psi_a(x)$
- $V(x) \propto x^2$ is an even function. So the energy eigenstates must be either even or odd. An odd function would have a node, thus increasing the energy. So our ansatz was chosen as an even function of x .

- Now $\langle p^2 \rangle = \frac{\hbar^2}{4a^2}$ and $\langle x^2 \rangle = a^2$ (show this using $\int x^2 e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\pi/\alpha^3}$). Up to numerical factors these formulae follow from dimensional analysis. Thus we get

$$E(a) = \langle H \rangle = \frac{\langle p^2 \rangle}{2m} + \frac{1}{2} m \omega^2 \langle x^2 \rangle = \frac{\hbar^2}{8ma^2} + \frac{1}{2} m \omega^2 a^2. \quad (7)$$

The minimum of $E(a)$ occurs when

$$\frac{\partial E(a)}{\partial a} = m\omega^2 a - \frac{\hbar^2}{4ma^3} = 0 \Rightarrow a^2 = \frac{\hbar}{2m\omega}. \quad (8)$$

So among the gaussian wave functions, the one with least energy is

$$\psi_o(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2} = \frac{\sqrt{\kappa}}{\pi^{1/4}} e^{-\frac{1}{2}\kappa^2 x^2}, \quad \kappa = \sqrt{\frac{m\omega}{\hbar}}, \quad A = \frac{\sqrt{\kappa}}{\pi^{1/4}} \quad (9)$$

Putting this a in $\langle H \rangle$, our variational estimate (upper bound) for the ground state energy is $E_0 = \frac{1}{2} \hbar \omega$. It turns out that this estimate is exact, and the true ground state wave function is as above! So one cannot reduce the energy by choosing some other functional form for our variational ansatz. For e.g. a Lorentzian $\psi_a(x) = \frac{A}{x^2+a^2}$ leads to a larger estimate for the ground state energy.

- We introduced $\kappa = \sqrt{\frac{m\omega}{\hbar}}$ which is a constant with dimensions of inverse length. κ controls the rate of decay of the position space probability distribution. The larger κ is, the less probable

it is to find the particle far from the point of equilibrium $x = 0$. $\kappa^2 = \frac{\sqrt{mk}}{\hbar}$ is large if the force constant k or mass is large, both of which prevent the particle from going far from $x = 0$. This is true both quantum mechanically as well as classically, so this observation has nothing to do with the size of \hbar .

2.3 Variational approximation for g.s. of anharmonic oscillator

Consider the anharmonic oscillator $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 + gx^4$. We wish to get a variational upper bound for the g.s. energy using the normalized trial wave function (α is a variational parameter.)

$$\psi(x) = Ae^{-\alpha x^2/2}, \quad A = \left(\frac{\alpha}{\pi}\right)^{1/4}, \quad \alpha > 0, g > 0, m > 0, \omega > 0. \quad (10)$$

1. Find the expectation value $\langle H \rangle$ in the trial state. Show that you get

$$\langle H \rangle = \frac{\hbar^2\alpha}{4m} + \frac{m\omega^2}{4\alpha} + \frac{3g}{4\alpha^2}. \quad (11)$$

Use $I = \int e^{-\alpha x^2} = \sqrt{\pi/\alpha}$, $\int x^2 e^{-\alpha x^2} dx = \frac{1}{2}\sqrt{\pi/\alpha^3}$ and $\int x^4 e^{-\alpha x^2} dx = (3/4)\sqrt{\pi/\alpha^5}$

2. Show that the optimal value of α is determined by the condition

$$f(\alpha) = \frac{\hbar^2}{m}\alpha^3 - m\omega^2\alpha - 6g = 0 \quad (12)$$

Argue that there is precisely one positive root α^* of this cubic equation.

Plot f . $f(\pm\infty) = \pm\infty$, $f(0) < 0$ and $f'(0) < 0$. f' vanishes at two points symmetrically located on either side of the vertical axis. So f must have precisely one positive zero. Can also arrive at this using Descartes rule of signs, there is only one change in sign of the non-zero coefficients arranged in standard form. There may be either two non-real roots or two more real roots which must be negative.

3. For the numerical values $\hbar = 1, m = 1, \omega = 1, g = \frac{1}{10}$ find the variational estimate E_0^V for g.s. energy. You may use the fact that the positive zero of $\alpha^3 - \alpha - 6g = 0$ occurs at $\alpha_* = 1.2212$ when $g = 1/10$. You should find $E_0^V = 0.56$
4. Recall that the g.s. energy to first order in perturbation theory around the SHO is

$$E_0^P = \frac{1}{2}\hbar\omega + \frac{3g\hbar^2}{4m^2\omega^2} + \dots \quad (13)$$

For the same numerical values find the g.s. energy E_0^P by 1st order perturbation theory. Answer: $E_0^P = \frac{1}{2} + \frac{3}{40} = \frac{23}{40} = 0.575$.

3 Perturbation theory for stationary states of time-independent Hamiltonians

In some cases, the Hamiltonian of interest can be written as $H = H_0 + gH_1$ where H_0 is 'exactly solved' and gH_1 is a 'perturbation'. In some situations, it may be possible to treat

the perturbation as small and develop an expansion in powers of g for the energy levels and eigenstates of H by using those of H_0 as a zeroth-order approximation. This approach is applied for example in studying the effect of an anharmonic restoring force on a particle in an SHO potential: here $gH_1 = gx^4$. The hydrogen atom in a constant magnetic field $gH_1 = g\vec{L} \cdot \vec{B}$ is another example. Relativistic corrections to the hydrogen atom Hamiltonian including the spin-orbit coupling $gH_1 = g\vec{L} \cdot \vec{S}$ can also be treated as a perturbation. An anisotropic rigid body can be treated as a perturbation to a rigid body with an axis of symmetry. The ground state energy of the Helium atom can be estimated by treating the inter-electron repulsion as a perturbation.

- There is another branch of perturbation theory that deals with time-dependent perturbations. This is relevant, for instance, if an atom is exposed to an oscillating electromagnetic field.
- In effect the method produces an expansion for the energy levels and stationary states of $H = H_0 + gH_1$:

$$E_n = E_n^{(0)} + E_n^{(1)}g + E_n^{(2)}g^2 + \dots \quad \text{and} \quad \psi_n = \psi_n^{(0)} + \psi_n^{(1)}g + \psi_n^{(2)}g^2 + \dots \quad (14)$$

where $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ is the energy spectrum of the unperturbed Hamiltonian H_0 .

3.1 Perturbation theory in a simple two state system

Perhaps the simplest instructive example of a perturbative expansion is for an electron spin in a magnetic field $\vec{B} = (B_x, B_y, B_z)$. Here the Hamiltonian $H = -\mu \cdot B$ is

$$H = \frac{g|e|\hbar}{4m} \vec{\sigma} \cdot \vec{B} = \frac{g|e|\hbar}{4m} \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}. \quad (15)$$

Here we can treat the magnetic interaction due to the field in the $x - y$ plane as a perturbation to the spin in the vertical magnetic field and split the Hamiltonian as $H_0 + H_1$ where (the so-called g -factor according to Dirac's theory of the electron is $g \approx 2$)

$$H_0 = \frac{g|e|\hbar B_z}{4m} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad H_1 = \frac{g|e|\hbar}{4m} \begin{pmatrix} 0 & B_x - iB_y \\ B_x + iB_y & 0 \end{pmatrix}. \quad (16)$$

In this case we may read off the energies and stationary states of H_0 and treat H_1 as a perturbation. We will develop a systematic method to calculate corrections to the energies and wavefunctions in the next section. But this problem is so simple that we can solve it explicitly. To avoid writing all the physical constants, let us consider the toy hermitian Hamiltonian $H = H_0 + gH_1$ where

$$H_0 = \begin{pmatrix} a & 0 \\ 0 & d \end{pmatrix} \quad \text{and} \quad gH_1 = g \begin{pmatrix} 0 & b \\ b^* & 0 \end{pmatrix}. \quad (17)$$

Here a, d are real and b is a complex number. g is called a coupling constant and can be regarded as measuring the size of the perturbation.

- The eigenvalues of H_0 are a and d with eigenvectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ respectively.
- The characteristic equation $\det(H - EI) = 0$ allows us to calculate the two energy levels

$$E^2 - (a + d)E + ad - g^2|b|^2 = 0 \quad \Rightarrow \quad E_{\pm} = \frac{1}{2} \left(a + d \pm \sqrt{(a + d)^2 - 4(ad - g^2|b|^2)} \right). \quad (18)$$

Find the corresponding eigenvectors! So far we have made no approximation.

- To understand the nature of a perturbative expansion, let us expand E_{\pm} around the eigenvalues of the unperturbed Hamiltonian using the binomial expansion for the square-root

$$E_{\pm} = \frac{a+d}{2} \pm \frac{1}{2} \sqrt{(a-d)^2 + 4g^2|b|^2} = \frac{a+d}{2} \pm \frac{a-d}{2} \left(1 + \frac{2g^2|b|^2}{(a-d)^2} + \dots \right) = \begin{cases} a + \frac{g^2|b|^2}{(a-d)} + \dots \\ d - \frac{g^2|b|^2}{(a-d)} + \dots \end{cases} \quad (19)$$

This expansion for $\sqrt{1+x^2}$ is valid (converges) when $|x| < 1$

$$\left| \frac{2gb}{a-d} \right| < 1 \quad (20)$$

The physical interpretation is that such a perturbation series provides a good approximation only if (1) the coupling constant g and (2) size of matrix elements of the perturbing Hamiltonian in the eigen-basis of H_0 ($|b|$) are sufficiently small and (3) the difference between the unperturbed levels $a-d$ is sufficiently large. If the energy levels of the unperturbed H_0 were degenerate, these series expansions would not be useful. These are general features of such ‘non-degenerate’ perturbative expansions.

- However, even if H_0 had degenerate energy levels $a=d$, we could still get a perturbation series, but of a different sort. If $a=d$, going back to E_{\pm} we find the exact formula

$$E_{\pm} = a \pm g|b|. \quad (21)$$

We see that the perturbing Hamiltonian gH_1 breaks the degeneracy of unperturbed levels by an amount proportional to g and the size of the matrix elements of H_1 (namely b). This is generally true. The degeneracy (in magnetic quantum number m) of hydrogen energy levels can be broken by applying a constant magnetic field.

3.2 First order non-degenerate perturbation theory

More generally, suppose we split the Hamiltonian $H = H_0 + gH_1$ into an unperturbed (hermitian) H_0 whose spectrum is known and a perturbation gH_1 . For example H_0 could be the Hamiltonian of Helium (2 electrons and α -particle) ignoring inter-electron repulsion while gH_1 is the Coulomb repulsion between electrons. Perturbation theory may be used to estimate the separation between ortho- and para-helium energy levels.

We will attempt to obtain the energy levels and eigenstates of H as series in powers of g

$$E_n = E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + \dots \quad \text{and} \quad \psi_n = \psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots \quad (22)$$

where $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. Our aim is to find the first order corrections $E_n^{(1)}$ and $\psi_n^{(1)}$. Roughly, we might expect that any change to $\psi_n^{(0)}$ that is in the direction of $\psi_n^{(0)}$ would not change the physical state and can be ignored. In other words, we expect to be able to take $\psi_n^{(1)}$ orthogonal to $\psi_n^{(0)}$. This is indeed the case.

More precisely, let us assume that the unperturbed states are normalized $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$ and choose to normalize the perturbed eigenstates as well. To order g , the normalization condition reads

$$1 \approx \langle \psi_n^0 + g\psi_n^1 | \psi_n^0 + g\psi_n^1 \rangle = \langle \psi_n^0 | \psi_n^0 \rangle + g\langle \psi_n^1 | \psi_n^0 \rangle + g\langle \psi_n^0 | \psi_n^1 \rangle + \mathcal{O}(g^2) \Rightarrow \Re\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 0 \quad (23)$$

So the real part of the inner product vanishes. In fact, by a choice of phase, we can also take the imaginary part of the inner product to vanish, i.e. $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$!²

- Now the eigenvalue problem for H becomes

$$(H_0 + gH_1) (\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots) = (E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + \dots) (\psi_n^{(0)} + g\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots).$$

At the lowest order g^0 this reduces to the unperturbed eigenvalue problem $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$. At $\mathcal{O}(g)$,

$$H_0\psi_n^{(1)} + H_1\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}. \quad (26)$$

To isolate $E_n^{(1)}$ let us take the inner product with $\psi_n^{(0)}$,

$$\langle \psi_n^{(0)} | H_0 | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle. \quad (27)$$

Using orthogonality of $\psi_n^{(0)}$ and $\psi_n^{(1)}$ and hermiticity of H_0 we get

$$E_n^{(1)} = \frac{\langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle}{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle} \Rightarrow E_n = E_n^{(0)} + g \frac{\langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle}{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle} + \dots \quad (28)$$

So to first order in perturbation theory, the correction to energy levels is given by the expectation value of the perturbing Hamiltonian in the unperturbed state.

- Remark: As a consequence of the variational principle, we notice that first order perturbation theory never underestimates the ground state energy:

$$E_0^{1\text{st order}} = E_0^0 + g \langle \psi_0^0 | H_1 | \psi_0^0 \rangle = \langle \psi_0^0 | H_0 + gH_1 | \psi_0^0 \rangle \geq E_0. \quad (29)$$

Here the exact ground state satisfies $H\psi_0 = E_0\psi_0$. By the variational principle E_0 is the minimum of the expectation value of the Hamiltonian

$$E_0 = \min_{\|\psi\|=1} \langle \psi | H_0 + gH_1 | \psi \rangle. \quad (30)$$

3.2.1 First order correction to the eigenstates

- To find $\psi^{(1)}$, it suffices to know its components in any basis. A convenient basis is the orthonormal basis of unperturbed energy eigenstates $\psi_m^{(0)}$. So we wish to express

$$|\psi_n^{(1)}\rangle = \sum_m \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle |\psi_m^{(0)}\rangle. \quad (31)$$

²Suppose $\Im \langle \psi^{(0)} | g\psi^{(1)} \rangle = cg$ for some constant c . Then

$$\langle \psi^{(0)} | g\psi^{(1)} \rangle = icg \approx e^{icg} - 1. \quad (24)$$

Now we may split ψ into a part parallel to $\psi^{(0)}$ and a part perpendicular to it. At order g

$$|\psi\rangle = |\psi^{(0)}\rangle + \langle \psi^{(0)} | g\psi^{(1)} \rangle |\psi^{(0)}\rangle + g|\psi_{\perp}^{(1)}\rangle + \dots \approx e^{icg} |\psi^{(0)}\rangle + g|\psi_{\perp}^{(1)}\rangle + \dots \quad (25)$$

By multiplying $|\psi\rangle$ by the phase e^{-icg} (which does not change its normalization) we may get rid of the phase factor from the first term without affecting the second term to order g . Thus, we may assume that the first order correction to the eigenstates are orthogonal to the unperturbed eigenstates $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$.

The aim is to find the coefficients in this expansion. We already saw in the last section that $\psi_n^{(1)}$ can be chosen not to have any component in the direction of $\psi_n^{(0)}$, so we restrict the sum above to run over $m \neq n$.

- To find $\psi_n^{(1)}$ we return to the eigenvalue equation at order g

$$H_0\psi_n^{(1)} + H_1\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}. \quad (32)$$

Taking the inner product with the m^{th} eigenstate of the unperturbed Hamiltonian we get

$$\begin{aligned} \langle \psi_m^{(0)} | H_0 \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H_1 \psi_n^{(0)} \rangle &= \langle \psi_m^{(0)} | E_n^{(0)} \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | E_n^{(1)} \psi_n^{(0)} \rangle \\ \Rightarrow E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle &= E_n^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle. \end{aligned} \quad (33)$$

In the last section, we studied the consequences of this equation when $m = n$ and concluded that $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$, i.e., $\psi_n^{(1)}$ has no component in the direction of $\psi_n^{(0)}$. To find its remaining components, we assume $m \neq n$ and that the unperturbed levels are non-degenerate and get

$$\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \frac{\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad \text{for } m \neq n. \quad (34)$$

Thus assuming $E_m^{(0)} \neq E_n^{(0)}$ for $m \neq n$, we find

$$\psi_n = \psi_n^{(0)} + g\psi_n^{(1)}, \quad \text{where } \psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle \psi_m^{(0)}}{E_n^{(0)} - E_m^{(0)}}. \quad (35)$$

So the first order correction to the unperturbed eigenstates is a linear combination of unperturbed eigenstates, weighted by the quotient of the matrix elements of H_1 between unperturbed states and the energy differences $E_n^{(0)} - E_m^{(0)}$. If the unperturbed energy levels $E_n^{(0)} = E_m^{(0)}$ were degenerate, this formula would run into difficulties if $\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle \neq 0$. As long as the unperturbed energy level of interest (n) is non-degenerate, the terms in this sum make sense (for instance, other levels could be degenerate and the formula would still work). So we still need to develop a formula for perturbative corrections to energy levels that are degenerate. We will do this shortly.

- Note also that for fixed n the terms in this sum over m eventually involve division by successively larger energy differences. So we might expect the projections of $\psi_n^{(1)}$ on the highly excited unperturbed states $\psi_m^{(0)}$ to be negligible, provided the matrix elements in the numerator $\langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle$ do not grow too fast with growing m .

3.3 Second order correction to the energy

At second order in g the eigenvalue equation becomes

$$H_0\psi_n^2 + H_1\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0. \quad (36)$$

As before, we look at this equation in the orthonormal basis of unperturbed eigenstates by taking the inner product with ψ_m^0 . Using hermiticity of H_0 we get

$$\langle \psi_m^0 | H_1 \psi_n^1 \rangle = E_n^2 \delta_{mn} + E_n^1 \langle \psi_m^0 | \psi_n^1 \rangle \quad (37)$$

Specializing to the case $m = n$ allows us to extract E_n^2 since $\langle \psi_n^0 | \psi_n^1 \rangle = 0$ by a choice of phase:

$$E_n^2 = \langle \psi_n^0 | H_1 \psi_n^1 \rangle \quad (38)$$

Now we substitute the known expression

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H_1 | \psi_n^0 \rangle \psi_m^0}{E_n^0 - E_m^0} \quad (39)$$

to get

$$E_n^{(2)} = \sum_{m \neq n} \frac{\langle \psi_m^0 | H_1 | \psi_n^0 \rangle \langle \psi_n^0 | H_1 | \psi_m^0 \rangle}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H_1 | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \quad (40)$$

We notice that the second order correction to the ground state energy $E_0^{(0)}$ is always negative. This is because the numerators are all absolute squares while the denominators are negative $E_0^0 - E_m^0 < 0$

$$E_{gs}^{(2)} \leq 0. \quad (41)$$

Summary: To second order in the coupling constant, the energy levels are

$$E_n(g) = E_n^0 + g \langle \psi_n^0 | H_1 | \psi_n^0 \rangle + g^2 \sum_{m \neq n} \frac{|\langle \psi_m^0 | H_1 | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} + \dots \quad (42)$$

3.4 Example: Point-like scatterer in a square-well potential

Let us illustrate perturbative approximations to energy levels with the example of a particle in a 1-dimensional infinite square-well, perturbed by a repulsive delta function. $H = H_0 + gH_1$

$$H_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x), \quad gH_1 = g\delta\left(x - \frac{L}{2}\right), \quad V(x) = \begin{cases} 0 & \text{if } 0 < x < L \\ \infty & \text{otherwise} \end{cases} \quad (43)$$

g has dimensions of Energy $\times L$. The unperturbed Hamiltonian is parity even about $x = L/2$, and so the unperturbed energy eigenstates are either even or odd about $x = L/2$. The unperturbed spectrum is non-degenerate

$$E_n^{(0)} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad \psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \dots \quad (44)$$

$n = 1, 3, 5$ correspond to the even states and $n = 2, 4, 6 \dots$ to the odd parity states. The first order correction to the energies

$$E_n^{(1)} = \langle \psi_n^{(0)} | \delta(x - L/2) | \psi_n^{(0)} \rangle = \frac{2}{L} \sin^2(n\pi/2) = \frac{1 - (-1)^n}{L} \quad (45)$$

vanishes for the odd parity states since they vanish where the delta scatterer is located. Thus within the approximation of first order perturbation theory

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} + \frac{2g}{L} \delta_{n,\text{odd}} \quad (46)$$

The second order correction to energies is

$$E_n^{(2)} = \sum_{p \neq n} \frac{|\langle \psi_p^{(0)} | H_1 | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_p^{(0)}} = \sum_{n \neq p=1}^{\infty} \frac{\sin^2(p\pi/2) \sin^2(n\pi/2) 8m}{(n^2 - p^2) \pi^2 \hbar^2} = \frac{2m}{\pi^2 \hbar^2} \sum_{n \neq p=1}^{\infty} \frac{1 - (-1)^n - (-1)^p + (-1)^{n+p}}{n^2 - p^2}. \quad (47)$$

Specializing we find that the second order correction to the ground state energy is negative and equal to³

$$E_1^{(2)} = -\frac{8m}{\pi^2 \hbar^2} \left[\frac{1}{3^2 - 1} + \frac{1}{5^2 - 1} + \frac{1}{7^2 - 1} + \dots \right] = -\frac{8m}{\pi^2 \hbar^2} \sum_{n=1}^{\infty} \frac{1}{4n(n+1)} = -\frac{2m}{\pi^2 \hbar^2} \quad (48)$$

Thus to second order in perturbation theory, the ground state energy of the perturbed Hamiltonian is

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} + \frac{2g}{L} - \frac{2mg^2}{\pi^2 \hbar^2} + \mathcal{O}(g^3) \quad (49)$$

Check that the dimensions are correct.

- To understand the quantitative accuracy of this perturbative approximation, let us compare with the exact ground state energy.
- To find the exact energy levels, we solve the Schrodinger equation in the above potential. The boundary conditions are

$$\psi(x \leq 0) = \psi(x \geq L) = 0, \quad \psi\left(\frac{L^+}{2}\right) = \psi\left(\frac{L^-}{2}\right), \quad \psi'\left(\frac{L^+}{2}\right) - \psi'\left(\frac{L^-}{2}\right) = \frac{2mg}{\hbar^2} \psi\left(\frac{L}{2}\right) \quad (50)$$

Like H_0 , the total H is also even about $L/2$, so its eigenstates can be taken as either even or odd. The odd parity states $n = 2, 4, 6, \dots$ of the unperturbed H_0 automatically satisfy these boundary conditions and are seen to be eigenstates of H since they satisfy the free particle Schrodinger equation both to the left and right of the delta scatterer. But the ground state of H is an even parity state which we now determine.

- For $x < L/2$ the solution of the Schrodinger eigenvalue problem with energy $E = \hbar^2 k^2 / 2m$ is $\psi = A \sin kx + B \cos kx$, imposing $\psi(0) = 0$ we get $\psi = A \sin kx$. Thus, the even parity wave functions are

$$\psi_{\text{even}}(x) = \begin{cases} A \sin kx & \text{if } 0 \leq x \leq L/2 \\ A \sin(k(L-x)) & \text{if } L/2 \leq x \leq L. \end{cases} \quad (51)$$

A will be fixed by normalization and it remains to find the allowed values of k . The continuity of ψ at $L/2$ is guaranteed but the condition on discontinuity of the derivative gives us the condition

$$-Ak \cos(kL/2) - Ak \cos(kL/2) = \frac{2mg}{\hbar^2} A \sin(kL/2) \quad (52)$$

This leads to the transcendental equation

$$-\frac{\hbar^2 k}{mg} = \tan\left(\frac{kL}{2}\right) \quad \text{or} \quad -\kappa = \alpha \tan \kappa, \quad \text{where} \quad \alpha = \frac{mgL}{2\hbar^2} > 0 \quad \text{and} \quad \kappa = \frac{kL}{2}. \quad (53)$$

The allowed energies correspond to solutions $\kappa \neq 0$ of this transcendental equation. The ground state corresponds to the smallest non-trivial solution $\pi/2 \leq \kappa_1 \leq \pi$ as is seen graphically.

³The series is seen to be telescoping when we use partial fractions $\frac{1}{n(n+1)} = \frac{1}{n} - \frac{1}{n+1}$

- For a quantitative test of perturbation theory, let us restrict to the ground state and use the values

$$\hbar = 1, m = 2, L = 1, g = 1, \alpha = 1. \quad (54)$$

In this case we find that $\kappa_1 \approx 2.02876$ and $k_1 \approx 4.06$ and

$$E_1^{exact} = \frac{\hbar^2 k_1^2}{2m} \approx 4.11586 \quad (55)$$

- On the other hand, our perturbative approximation for the ground state energy is

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} + \frac{2g}{L} - \frac{2mg^2}{\pi^2 \hbar^2} + \mathcal{O}(g^3) = \frac{\pi^2}{4} + 2 - \frac{4}{\pi^2} + \dots = 2.4674 + 2 - .405 + \dots = 4.06212 + \dots \quad (56)$$

Thus we see that second order perturbation theory gives an estimate of the ground state energy 4.062 which is within 1.3% of the exact ground state energy ≈ 4.116 ! If g were smaller, the accuracy of perturbation theory would be even better. Moreover we notice that first order perturbation theory ($E_1^{\text{1st order}} \approx 4.46$) overestimates the energy of the g.s. while the second order correction is negative.

3.5 First order degenerate perturbation theory

Suppose $H = H_0 + gH_1$ and we wish to find the correction to a degenerate energy level $E_n^{(0)}$ of H_0 . Since it is degenerate there are several linearly independent eigenvectors of H_0 with eigenvalue $E_n^{(0)}$. In fact, H_0 is diagonal in *any* basis within the $E_n^{(0)}$ eigenspace. For convenience let us work with orthonormal bases and denote one such orthonormal basis by $\psi_{n\alpha}^0$ where $\alpha = \alpha(n)$ enumerates the degenerate levels

$$H_0 \psi_{n\alpha}^0 = E_n^{(0)} \psi_{n\alpha}^0 \quad (57)$$

Of course, $\psi_{n\alpha}$ are not uniquely determined by H_0 . We will see that the perturbation H_1 helps us to determine the ‘right’ basis within the degenerate subspace. Moreover, we expect the perturbation H_1 to break the degeneracy among the unperturbed levels, since it was found that application of a magnetic field ‘splits’ the degenerate energy levels of hydrogen.

- We wish to expand the energies and eigenstates of H in a series in g

$$E_{n\alpha} = E_n^{(0)} + E_{n\alpha}^1 g + E_{n\alpha}^2 g^2 + \dots \quad \psi_{n\alpha} = \psi_{n\alpha}^0 + \psi_{n\alpha}^1 g + \psi_{n\alpha}^2 g^2 + \dots \quad (58)$$

Now we can’t just take over the formula for $E_n^1 = \langle \psi_n^0 | H_1 | \psi_n^0 \rangle$ from non-degenerate perturbation theory since we do not know which of the states $\psi_{n\alpha}^0$ to calculate this expectation value in.

- The eigenvalue problem $H \psi_{n\alpha} = E_{n\alpha} \psi_{n\alpha}$ is (the super-scripts on ψ and E are not powers!)

$$(H_0 + gH_1) (\psi_{n\alpha}^0 + g\psi_{n\alpha}^1 + g^2\psi_{n\alpha}^2 + \dots) = (E_{n\alpha}^0 + gE_{n\alpha}^1 + g^2E_{n\alpha}^2 + \dots) (\psi_{n\alpha}^0 + g\psi_{n\alpha}^1 + g^2\psi_{n\alpha}^2 + \dots).$$

At order g^0 this just says that α labels the degenerate levels with energy E_n^0 :

$$H_0 \psi_{n\alpha}^0 = E_n^0 \psi_{n\alpha}^0. \quad (59)$$

Due to the degeneracy, we don’t know the states $\psi_{n\alpha}$ uniquely, but without much loss of generality, let us suppose the unperturbed eigenstates are orthonormal

$$\langle \psi_{m\beta}^0 | \psi_{n\alpha}^0 \rangle = \delta_{\alpha\beta} \delta_{mn}. \quad (60)$$

At order g^1 we get

$$H_0\psi_{n\alpha}^1 + H_1\psi_{n\alpha}^0 = E_n^0\psi_{n\alpha}^1 + E_{n\alpha}^1\psi_{n\alpha}^0 \quad (61)$$

As before, let us take the inner product with the unperturbed states $\psi_{m\beta}^0$. Using hermiticity of H_0 and orthonormality of unperturbed states we get

$$\langle\psi_{m\beta}^0|H_1|\psi_{n\alpha}^0\rangle = E_{n\alpha}^1\delta_{mn}\delta_{\alpha\beta} + (E_n^0 - E_m^0)\langle\psi_{m\beta}^0|\psi_{n\alpha}^1\rangle. \quad (62)$$

To find $E_{n\alpha}^1$ let us take $m = n$, i.e., focus on a particular degenerate eigenspace of H_0 . Then we have

$$\langle\psi_{n\beta}^0|H_1|\psi_{n\alpha}^0\rangle = E_{n\alpha}^1\delta_{\alpha\beta}. \quad (63)$$

Bear in mind that we have still not fixed the basis $\psi_{n\alpha}^0$ within the E_n^0 degenerate eigenspace, and nor do we know $E_{n\alpha}^1$. This interesting equation determines them both. It says that the basis $\psi_{n\alpha}^0$ is one in which H_1 is diagonal, and the diagonal entries are the first order corrections to the energy levels $E_{n\alpha}^1$. **In other words, $E_{n\alpha}^1$ are the eigenvalues of H_1 restricted to the degenerate E_n^0 eigenspace of H_0 . And $\psi_{n\alpha}^0$ are the corresponding eigenvectors.** This is the main result of 1st order degenerate perturbation theory.

3.5.1 Simplest example of Zeeman effect

The Zeeman effect refers to the experimentally observed shift in atomic energy levels in the presence of a uniform external magnetic field. Let us consider a very simple example of this effect⁴, where a hydrogen atom is placed in an external magnetic field. The magnetic dipole interaction energy is

$$H_{int} = -\boldsymbol{\mu} \cdot \mathbf{B} = \left(\frac{e}{2m}\vec{L} + \frac{e}{m}\vec{S}\right) \cdot \mathbf{B}. \quad (64)$$

Now the unperturbed Hamiltonian is just the hydrogen atom Hamiltonian $H_0 = \frac{\vec{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$ whose eigenstates are $|nlm_l\rangle \times$ a spin wave function which we may take to be $|sm_s\rangle$ where $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$

$$H_0|nlm_lsm_s\rangle = -\frac{R}{n^2}|nlm_lsm_s\rangle, \quad n = 1, 2, \dots, l = 0, 1, \dots, n-1, m = -l, \dots, l, m_s = -\frac{1}{2}, \frac{1}{2} \quad (65)$$

where $R = -me^4/2\hbar^2 = -13.6$ eV is the Rydberg energy. The energy levels are $2n^2$ -fold degenerate. We wish to find the correction to the energy levels due to the magnetic dipole interaction with the uniform external magnetic field, $H = H_0 + H_{int}$. Let us assume that the magnetic field is oriented along the z direction, $\mathbf{B} = B_z\hat{z}$. Now it is a fortunate circumstance that

$$H_{int} = \frac{e}{2m}(L_z + 2S_z)B_z \quad (66)$$

is diagonal in the basis of unperturbed energy levels:

$$H_{int}|nlm_lsm_s\rangle = \frac{e\hbar}{2m}(m_l + 2m_s)B_z|nlm_lsm_s\rangle \quad (67)$$

⁴We ignore here the effect of the internal magnetic field (due to the motion of the electron in the electric field of the nucleus).

So the diagonalization of the perturbed Hamiltonian within each degenerate subspace of H_0 has already been done. The exact energy eigenstates of $H_0 + H_{int}$ are $|nlm_l m_s\rangle$ with the energies

$$(H_0 + H_{int}) |nlm_l m_s\rangle = \left(-\frac{R}{n^2} + \frac{e\hbar}{2m} (m_l + 2m_s) B_z \right) |nlm_l m_s\rangle \quad (68)$$

Thus the unperturbed states with different values of m_l , m_s , which were degenerate in energy are now split in the presence of an external magnetic field. m_l is therefore called the magnetic quantum number.

4 Semiclassical (WKB) approximation

4.1 Semi-classical regime and slowly varying potentials

- Named after Wentzel, Kramers and Brillouin. We wish to approximately solve the time-independent Schrödinger equation for stationary states that are nearly classical.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x). \quad (69)$$

To do this, we wish to exploit the knowledge of some solution of the classical (Hamilton/Newton) equations of motion. In stationary perturbation theory, the zeroth order was a solution of the unperturbed problem. In the semi-classical approximation, the zeroth order is typically a classical solution (in an appropriate form). Classically, the particle is confined to the region x where $E \geq V(x)$. So we focus on this region and postpone phenomena like tunneling through barriers, which are classically forbidden.

- Let us recall which (stationary) states behave more classically than others. If the potential is a constant (as in an infinite square-well of length L in which $V = 0$), $\psi(x) = Ae^{ikx} + Be^{-ikx}$ where $k = \frac{\sqrt{2m(E-V)}}{\hbar}$ and the boundary conditions imply that the stationary states are $\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$. Classically, a particle with non-zero speed spends on average equal times in all subintervals of $[0, L]$ of equal length, as it bounces back and forth against the walls. This uniform distribution is approximated by the probability distribution $|\psi(x)|^2$ of highly excited states. So the classical limit here is the limit of high energies ($E_n \gg V$). This is also the limit of large wave number $k_n = \frac{n\pi}{L}$ compared to $\frac{1}{L}$. This is also the limit where the de Broglie wave length $\lambda_{dB} = \frac{h}{\sqrt{2m(E-V)}} = \frac{2\pi}{k_n} = \frac{2L}{n}$ is small compared to L .

- Notice that L here is the length scale over which the potential changes significantly. More generally, if $V = V(x)$ we say we are in the semi-classical regime if the de Broglie wave length is small compared to the length scale over which the potential varies significantly.

- This is the case, for example for a highly excited state of a particle in an SHO potential. As long as we stay away from the classical turning points, the wave function oscillates rapidly and its wavelength is small. Near the turning points, λ_{dB} diverges and the quantum effects have to be treated more carefully.

- If the potential is varying slowly with x , we may still surmise that the wave function is of the form $Ae^{\pm ipx/\hbar}$ but that $p = h/\lambda$ is no longer the constant $\hbar k$, but varies slowly with x . In other words, this suggests the ansatz $\psi \sim e^{iS(x)/\hbar}$ where for a constant potential, $S(x) = px =$

$\pm x\sqrt{2m(E-V)}$. Before we work out the consequences of this ansatz, let us say more on what we mean by the semi-classical regime and what it means for the potential to be slowly varying.

- If $V = V(x)$, we require that the wavelength is small compared to the length scale over which the potential changes by an amount of the order of the kinetic energy of the particle⁵. Indeed, suppose the potential changes by $p^2/2m$ over a length L , then⁶

$$\frac{p^2}{2m} \approx \delta V \approx \left| \frac{dV}{dx} \right| L \quad \Rightarrow \quad L \approx \frac{p^2}{2m} \left| \frac{dV}{dx} \right|^{-1} \quad (70)$$

Now

$$\lambda \ll L \quad \Rightarrow \quad \frac{2m\lambda}{p^2} \left| \frac{dV}{dx} \right| \ll 1 \quad \text{or} \quad \left| \frac{2mh}{p^3} \frac{dV}{dx} \right| \ll 1 \quad \text{or} \quad \left| \frac{dV}{dx} \right| \ll \frac{\sqrt{2m}}{h} |E - V(x)|^{\frac{3}{2}} \quad (71)$$

This is our condition for semi-classical behavior. It is a condition on the potential, that also involves the energy and depends on x . It is easier to satisfy this condition for a fixed potential and x , if we make E bigger: excited states behave more classically. It is easier to satisfy (for fixed E) where dV/dx is ‘small’. The criterion involves x , so even for fixed $V(x)$ and E there may be some locations where the behavior *is* semi-classical ($E \gg V(x)$), and other locations where it is *not* semi-classical ($E \approx V(x)$). Also, the ‘smaller’ \hbar is, the easier it is to satisfy this condition so in a sense $\hbar \rightarrow 0$ is the classical limit.

- Let us re-derive this condition by thinking in terms of the de Broglie wavelength. For a non-constant $V(x)$, the de Broglie wavelength changes with x . The concept of a wavelength is useful if there are many oscillations with roughly the same wavelength. This is the case if the change in wavelength (over a length of one wavelength) is small compared to the wavelength itself. The change in wavelength over a distance δx is

$$\delta\lambda = \frac{d\lambda}{dx} \delta x. \quad (72)$$

So putting $\delta x = \lambda$, the change in wavelength over a wavelength is $\delta\lambda = \frac{d\lambda}{dx} \lambda$. Thus we require $\left| \frac{\delta\lambda}{\lambda} \right| = \left| \frac{d\lambda}{dx} \right| \ll 1$. We can express this as a condition on the potential using $\lambda = h/\sqrt{2m(E-V(x))}$.

$$\left| \frac{\delta\lambda}{\lambda} \right| = \left| \frac{mh}{p^3} \frac{dV}{dx} \right| \ll 1 \quad (73)$$

This is the same condition for semi-classicality as obtained earlier. So we can either say the potential is slowly varying or the de Broglie wavelength is slowly varying.

⁵We need to decide what we mean by potential ‘changes appreciably’. The change in the potential has dimensions of energy and the KE of the particle is a reasonable scale of energy to compare with. Indeed, near the turning points of the SHO, the KE is small, so the length scale over which the potential changes by an amount of the order of the KE is quite small. On the other hand, far away from the turning points the KE is large (for a highly excited state), and the length scale over which the potential changes appreciably compared to the KE is large. So by this definition, the SHO potential is slowly-varying away from the turning points for a highly excited state, and not slowly-varying near the turning points. The corresponding statement about the smallness/largeness of λ_{dB} is a consequence since $\lambda = h/\sqrt{2m(E-V(x))}$ is determined by E and $V(x)$.

⁶In approximating δV by its first derivative, we assume that L is not so large that this approximation breaks down.

4.2 Method of variation of constants for a slowly varying potential

• We motivated the ansatz $\psi = Ae^{iS(x)/\hbar}$ in seeking a solution of the time-independent Schrödinger equation in the semi-classical regime. Without further assumptions, this ansatz (for complex S and real A), does not involve any approximation, it is merely a change of dependent variable from $\psi(x)$ to $S(x)$, in terms of which the eigenvalue problem becomes

$$-\frac{\hbar^2}{2m}\psi'' = (E - V)\psi \quad \Rightarrow \quad -\frac{i\hbar}{2m}S'' + \frac{1}{2m}(S')^2 + V(x) = E. \quad (74)$$

Now we exploit the slowly varying nature of $V(x)$ to assume that $S'(x)$ is slowly varying⁷ so that we may ignore $S''(x)$ and approximate the SE by

$$\frac{1}{2m} \left(\frac{\partial S}{\partial x} \right)^2 + V = E \quad (75)$$

Notice that this approximation could also be obtained by letting $\hbar \rightarrow 0$ (assuming $S(x)$ has a finite limit as $\hbar \rightarrow 0$), more on this later. Moreover, the resulting equation is the time-independent Hamilton-Jacobi equation of classical mechanics for the distinguished generating function \mathcal{S} of a canonical transformation $\mathcal{S}(x, P, t) = S(x, P) - Et$ from ‘old’ coordinates x, p to new coordinates X, P in which the new Hamiltonian $K(X, P) = H(x, p) + \frac{\partial \mathcal{S}}{\partial t} = 0$ vanishes identically. Note that the Hamiltonian appearing in the Schrödinger equation is the old Hamiltonian H , not K . Moreover, even though $K = 0$, this does not mean that the quantum mechanical energy levels are all zero, K is not a unitary transform of H , they do not have the same spectra. It is just that in the new coordinates ($Q = \frac{\partial \mathcal{S}}{\partial P}$ and P), the classical dynamics is as simple as it could be since X and P are both constants of motion $\dot{X} = \frac{\partial K}{\partial P} = 0$ and $\dot{P} = -\frac{\partial K}{\partial X} = 0$. All the complications of the original Hamiltonian have been dumped in the transformation from old coordinates (x and $p = \frac{\partial \mathcal{S}}{\partial x}$) to new coordinates (X and P). The generating function $S(x)$ in the above H-J equation in fact also depends on the new momenta P , though it is not apparent from (75). This dependence enters through the dependence of S on the constants of integration resulting from solving the time-dependent H-J partial differential equation. The constants of integration can be taken as the constant new momenta.

• In our context, we write the H-J equation in the form $S'(x)^2 = p^2$ and integrate to get

$$S(x) - S(x_0) = \pm \int_{x_0}^x p(x') dx' \quad \text{where} \quad p(x) = \sqrt{2m(E - V(x))}. \quad (76)$$

Thus, our crude approximation for the wave function in the semi-classical regime is essentially the exponential of an *abbreviated* action integral⁸

$$\psi(x) = Ae^{\frac{i}{\hbar} \int_{x_0}^x p(x') dx'} + Be^{-\frac{i}{\hbar} \int_{x_0}^x p(x') dx'}. \quad (77)$$

• We will improve on this approximation shortly. But even this crude approximation leads to some interesting consequences such as a simple case of the Bohr-Sommerfeld quantization condition.

⁷For a constant potential $S'(x) = \hbar k$ is a constant, so now we imagine that this erstwhile ‘constant’ varies with x .

⁸By absorbing a phase and its conjugate into A and B , the limit of integration x_0 may be set equal to the left turning point of the classical trajectory.

- Suppose a particle moves in the 1 dimensional potential $V(x)$ which becomes infinite for $x < 0$ and $x > L$ but is arbitrary for $0 \leq x \leq L$. Then the approximate wave function satisfying the boundary condition $\psi(0) = 0$ is

$$\psi(x) \approx A \sin\left(\frac{S(x)}{\hbar}\right) \quad \text{where} \quad S(x) = \int_0^x p(x') dx'. \quad (78)$$

The boundary condition $\psi(L) = 0$ then becomes $S(L) = n\pi\hbar$ which is the Bohr quantization condition

$$\oint p(x') dx' = 2 \int_0^L p(x') dx' = nh. \quad (79)$$

Use this condition to find a semi-classical approximation to the square-well energy levels.

- Let us continue with the theme of making constants vary. A simple way of improving on this approximation is to suppose that both the amplitude and phase are slowly varying functions. Let us put $\psi(x) = A(x)e^{iS(x)/\hbar}$ in the SE, where we now suppose that both $A(x)$ and $S(x)$ are real. We get

$$-\frac{\hbar^2}{2m} \left(A'' + \frac{i}{\hbar} (2A'S' + AS'') - \frac{AS'^2}{\hbar^2} \right) + V(x)A(x) = EA(x). \quad (80)$$

The real part gives us

$$-\frac{\hbar^2}{2m} \left(A'' - \frac{AS'^2}{\hbar^2} \right) = (E - V(x))A(x) \quad (81)$$

which reduces to the time-independent H-J equation, if we ignore the second derivative of $A(x)$. The solution is $S = \pm \int^x p(x') dx'$ as before. The imaginary part gives us the condition $2A'S' + AS'' = 0$ which means $(A^2S')' = 0$ or $A(x) = \pm \frac{C}{\sqrt{S'}} = \pm \frac{C}{\sqrt{p(x)}}$ for some constant C . The approximate wavefunction is

$$\psi(x) \approx \frac{C_1}{\sqrt{p(x)}} e^{i \int^x p(x') dx'} + \frac{C_2}{\sqrt{p(x)}} e^{-i \int^x p(x') dx'} \quad \text{where} \quad p(x) = \sqrt{2m(E - V(x))}. \quad (82)$$

This is already a better approximation. The contributing amplitudes are inversely proportional to $\sqrt{p(x)}$. So aside from interference effects, the particle is less likely to be found in a place where its classical velocity is large, as we observed for a particle near the equilibrium point in an SHO potential.

- It is possible to improve on this approximation by developing a systematic semi-classical expansion that incorporates effects of more rapid variation in the potential.

4.3 Examples and features of the semi-classical limit $\hbar \rightarrow 0$

- To get the Hamilton-Jacobi equation of classical mechanics from the Schrödinger equation, we let $\hbar \rightarrow 0$ after making the ansatz $\psi = Ae^{iS/\hbar}$. So we should expect classical behaviour to emerge in the limit $\hbar \rightarrow 0$.

- To reinforce this idea, let us look at the gaussian wave packet for a free particle in this limit. The probability density of a gaussian wave packet is

$$P(x, t) = |\psi(x, t)|^2 = \frac{1}{\sqrt{2\pi}a(t)} e^{-\frac{(x - \frac{p_0 t}{m})^2}{2a(t)^2}} \quad \text{where} \quad a(t) = a\sqrt{1 + \frac{t^2}{\tau^2}} \quad \text{and} \quad \tau = \frac{2ma^2}{\hbar} \quad (83)$$

τ is the characteristic time scale over which the wave packet broadens. The mean momentum of this wave packet is $\langle p \rangle = p_o = \hbar k_o$ and the mean position is $\langle x \rangle = \frac{p_o t}{m}$. We take the limit $\hbar \rightarrow 0$ holding p_o fixed (i.e. the limit of large wave number $k_o = \frac{p_o}{\hbar} \rightarrow \infty$). As $\hbar \rightarrow 0$, $\tau \rightarrow \infty$ and the wave packet does not broaden out. The dispersive effects of wave mechanics die out as $\hbar \rightarrow 0$ and the object behaves like a classical particle of fixed size a . To model a classical point-like particle, we could further let $a \rightarrow 0$ and get the probability density $P(x, t) = \delta(x - p_o t/m)$ as expected of a free point-like particle moving at velocity p_o/m .

- The limit $\hbar \rightarrow 0$ is a very convenient way of approaching the classical limit. \hbar is a dimensional constant, so what we mean by $\hbar \rightarrow 0$ is that certain physical quantities with dimensions of action are very large compared to \hbar . In the above example of a free particle gaussian wave packet, the relevant quantity with dimensions of action is $\frac{2ma^2}{t}$. So the classical limit is the one where we consider times t much shorter than the time-scale τ for quantum mechanical dispersive broadening of the wave packet.

- E.g. 3. For highly excited states of the harmonic oscillator, the quantity $\frac{E_n}{\omega} = \hbar(n + \frac{1}{2})$ with dimensions of action is large compared to \hbar . These states behave semi-classically in many respects.

- E.g. L^2 eigenstates of a rigid body with very large angular momentum quantum number $l \gg 1$ behave semi-classically, the magnitude of their total angular momentum $\sqrt{\hbar^2 l(l+1)}$ is the quantity with dimensions of action, that is large compared to \hbar .

- Spin is somewhat different from angular momentum. A given rigid body or atom can be in states of very different angular momentum quantum number l . So letting $\hbar \rightarrow 0$ and simultaneously $l \rightarrow \infty$ while holding the classical quantity $|\vec{L}| = \sqrt{\hbar^2 l(l+1)}$ fixed is a classical limit. On the other hand, an electron is always a spin $s = \frac{1}{2}$ particle, so for an electron, the eigenvalue of S^2 is always $3\hbar^2/4$ which is not large compared to \hbar^2 . So it does not make direct sense to let the spin quantum number s of an *electron* take any value other than $\frac{1}{2}$, leave alone let it go to infinity.

- However, the limit $\hbar \rightarrow 0$ is not a simple one. The wave function of a free particle $\psi(x) = Ae^{ipx/\hbar}$ does not have a good classical limit $\hbar \rightarrow 0$, holding the classically meaningful quantities x, p fixed. Indeed, the wave function has an essential singularity as $\hbar \rightarrow 0$. However, $-i\hbar \log \psi$ does have a good limit as $\hbar \rightarrow 0$, it tends to the abbreviated action px for a trajectory between positions 0 and x .

- In the case of the SHO, the stationary states are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega x^2}{2\hbar}} \quad (84)$$

Here too $\psi(x)$ has an essential singularity at $\hbar = 0$, but $\hbar \log \psi(x)$ has a finite limit $-\frac{m\omega x^2}{2}$ as $\hbar \rightarrow 0$.

4.4 Semi-classical expansion in powers of \hbar

- For a general potential, the above examples suggest it isn't a good idea to look for an expansion of $\psi(x)$ in powers of \hbar around a 'classical wave function', since such a thing does not even exist for a free particle. It is better to make the ansatz $\psi = Ae^{iS(x)/\hbar}$ and try to expand $S(x)$ in powers of \hbar . Thus we will seek a solution of the time-independent SE in the form $\psi = Ae^{iS(x, \hbar)/\hbar}$

where $S(x)$ is a (possibly complex) function of x depending on \hbar and A is a constant⁹. Then

$$\psi'(x) = \frac{iS'}{\hbar}\psi(x), \quad \psi''(x) = \left(\frac{iS''}{\hbar} - \frac{S'^2}{\hbar^2}\right)\psi(x) \quad (85)$$

and the SE becomes

$$-\frac{\hbar^2}{2m} \left(\frac{iS''}{\hbar} - \frac{S'^2}{\hbar^2}\right) + V(x) = E \quad (86)$$

Now we suppose $S(x)$ is expanded in a series in \hbar

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \dots \quad (87)$$

In effect, we are assuming that $S(x)$ has a finite limit as $\hbar \rightarrow 0$. This is true for the free particle as well as for the highly excited states of many problems we have solved (SHO, square well, delta potential). In fact it is true even for low lying states of many of the problems we have solved (like the SHO above). However, it is not always the case that $S(x, \hbar)$ has a finite limit as $\hbar \rightarrow 0$. Not all states are semi-classical. This is especially true for low lying states such as the ground state of the δ potential well or the hydrogen atom, where

$$\psi_0(x) = \frac{\sqrt{mg}}{\hbar} e^{-mg|x|/\hbar^2} \quad \text{and} \quad \psi_{100}(x) = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{me^2 r}{4\pi\epsilon_0 \hbar^2}} \quad \text{where} \quad a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}. \quad (88)$$

For both these ground states, $\hbar \log \psi$ does *not* have a finite limit as $\hbar \rightarrow 0$, though $\hbar^2 \log \psi$ has a finite limit. In both these cases, we anticipate that the above semi-classical approximation may not be accurate. On the other hand, the semi-classical expansion will be seen to be a good approximation in situations where our criterion for the semi-classical regime (slowly varying potential or de Broglie wavelength) is satisfied. In those situations, we may use solutions of the classical HJ equation to obtain accurate semi-classical wave functions.

- Note that we are not claiming that the expansion of $S(x, \hbar)$ in powers of \hbar is convergent. This is true for the free particle where $S(x) = px$. But for most potentials, even in the semi-classical regime, the expansion $S(x, \hbar) = S_0 + S_1\hbar + S_2\hbar^2 + \dots$ is *divergent*. Nevertheless, it does provide an excellent asymptotic approximation in many cases.

- Equating coefficients of like powers of \hbar , we get a sequence of differential equations for S_n . At order \hbar^0 we recover the time-independent H-J equation, which is the non-linear differential equation

$$\frac{S_0'(x)^2}{2m} + V(x) = E \quad (89)$$

with solution $S_0(x) = \pm \int_{x_0}^x \sqrt{2m(E - V(x'))} dx' = \pm \int_{x_0}^x p(x') dx'$. This is called the Eikonal approximation or the classical approximation. S_0 is called the Eikonal or (abbreviated) action or Hamilton's principal function.

- At order \hbar we get a linear equation for S_1 , into which we substitute the known $S_0' = p(x)$:

$$S_1'(x)S_0'(x) = \frac{i}{2}S_0'' \Rightarrow S_1'(x) = \frac{i}{2} \frac{S_0''}{S_0'} = \frac{i}{2} (\log S_0')' = \frac{i}{2} (\log p(x))' \Rightarrow S_1 = \frac{i}{2} \log p(x) + \text{const.}$$

⁹We were in effect beginning to do this when we previously made the ansatz $\psi(x) = A(x)e^{iS(x)/\hbar} = e^{\frac{i}{\hbar}(S(x) - i\hbar \log A(x))}$.

Thus we find at this order of approximation

$$\psi(x) \approx \frac{A_1}{\sqrt{p(x)}} e^{\frac{i}{\hbar} \int_{x_0}^x p(x') dx'} + \frac{A_2}{\sqrt{p(x)}} e^{-\frac{i}{\hbar} \int_{x_0}^x p(x') dx'}. \quad (90)$$

This matches our earlier result. But the present method is more systematic and allows us to find further quantum corrections around the classical limit! What is more, this method can also be applied to regions which the classical trajectory is forbidden from exploring (e.g. tunneling through a barrier).

- Let us find a condition for the validity of the eikonal approximation. Recall that we found upon substituting $S = S_0 + \hbar S_1 + \dots$ and $\psi = e^{iS/\hbar}$ in the Schrodinger eigenvalue problem

$$(S'_0)^2 + \hbar(2S'_0 S'_1 - iS''_0) + \mathcal{O}(\hbar^2) = 2m(E - V(x)). \quad (91)$$

Now for the Eikonal approximation to be good, the order of magnitude of the terms of order \hbar^0 must be large compared to that of the terms of order \hbar . $|(S_0')^2|$ can be taken as the order of magnitude of the constant terms in \hbar and $|i\hbar S''_0|$ the order of magnitude of the terms of linear in \hbar . So the condition is

$$|(S_0')^2| \gg |\hbar S''_0| \quad \text{or} \quad \left| \frac{\hbar S''_0}{S_0'^2} \right| \ll 1 \quad (92)$$

This is the same as our earlier criterion for the semi-classical regime, that the potential or de Broglie wavelength be slowly varying $\left| \frac{d\lambda}{dx} \right| \ll 1$:

$$\lambda(x) = \frac{h}{p(x)} = \frac{h}{S'_0} \Rightarrow \left| \frac{d\lambda}{dx} \right| = \left| \frac{h S''_0}{S_0'^2} \right| \ll 1 \quad (93)$$

4.5 Estimation of Tunneling amplitude

- Previously, we tried to use solutions of the classical Hamilton-Jacobi equation to approximately infer the quantum mechanical wave function. This program was applicable in the classically allowed region $E > V(x)$. On the other hand, the wave function can be non-zero even in classically forbidden regions ($E < V(x)$) as in the case of tunneling through a barrier. In such classically forbidden regions, we may still obtain a semiclassical approximation to the wavefunction using the expansion in powers of \hbar developed in the last section. Even if $E < V$, the condition for the semi-classical regime $\left| \frac{d\lambda}{dx} \right| \ll 1$ or $\left| \frac{dV}{dx} \right| \ll \frac{\sqrt{2m}}{\hbar} |E - V(x)|^{\frac{3}{2}}$ can still be satisfied, especially if $E \ll V$ or if $\frac{dV}{dx}$ is small.

- For simplicity let us consider scattering against a barrier in one dimension that extends between $x = -L$ and L , such as a rectangular barrier with an undulating top $V(x) > 0$ for $|x| \leq L$ and $V(x) = 0$ for $|x| > L$. Classically if the energy $E > V_{\max}$, the particle ‘rolls over’ the barrier, but is reflected otherwise. Quantum mechanically, even if $E < V_{\max}$ there can be a non-zero transmission probability due to tunneling. We wish to get a semi-classical estimate for the transmission coefficient in cases where it is small. (After all, it is zero classically.)

- Let us consider scattering from the left with incident energy $E = \hbar^2 k^2 / 2m < V_{\max}$. Suppose the repulsive potential is such that there are just two classical turning points ($x_L = -L$ on the left of the barrier and $x_R = L$ on the right) between which $V(x) > E$, as is the case for a rectangular barrier.

- In the classically allowed regions to the left ($\psi(x) = Ae^{ikx} + Be^{-ikx}$) and right ($\psi(x) = Fe^{ikx}$) of the barrier, the WKB approximation gives the exact free particle wave functions since the potential is a constant. The transmission coefficient we wish to find is $|F/A|^2$. Instead of trying to solve the SE in the classically disallowed region, we use the WKB approximation

$$\psi(x) \approx \frac{C'}{\sqrt{p(x)}} e^{\frac{i}{\hbar} \int_{x_L}^x p(x') dx'} + \frac{D'}{\sqrt{p(x)}} e^{-\frac{i}{\hbar} \int_{x_L}^x p(x') dx'} \quad (94)$$

Here $p(x) = \sqrt{E - V(x)}$ is purely imaginary and we may absorb some phases into C' and D' and write

$$\psi(x) \approx \frac{C}{\sqrt{|p(x)|}} e^{-\frac{1}{\hbar} \int_{x_L}^x \sqrt{2m(V(x') - E)} dx'} + \frac{D}{\sqrt{|p(x)|}} e^{\frac{1}{\hbar} \int_{x_L}^x \sqrt{2m(V(x') - E)} dx'}. \quad (95)$$

- Since we assumed the tunneling probability is small, the barrier must be high (compared to E) or wide (compared to the de Broglie wavelength of the incident wave). In this case, the coefficient D of the exponentially growing wavefunction must be very small and we ignore it ($D \rightarrow 0$ as the barrier width $L \rightarrow \infty$). This can be motivated by imposing continuity of $\psi(x)$ and its first derivative at the classical turning points x_L, x_R . The attenuation of the wavefunction is approximately

$$\frac{|F|}{|A|} \approx e^{-\frac{1}{\hbar} \int_{x_L}^{x_R} \sqrt{2m(V(x') - E)} dx'} \equiv e^{-\gamma} \quad (96)$$

So the WKB estimate for the transmission probability is

$$T \approx e^{-2\gamma} = e^{-\frac{2}{\hbar} \int_{x_L}^{x_R} \sqrt{2m(V(x') - E)} dx'} \quad (97)$$

We see that as $\hbar \rightarrow 0$, $T \rightarrow 0$ exponentially fast and classically the particle is not transmitted.

- Tunneling was used by Gamow and others to explain the decay of a nucleus to a daughter nucleus by emission of an α (npp) particle. The strong nuclear forces create something like an attractive finite spherical potential well inside the nucleus for the alpha particle. Outside the nucleus, the alpha particle is repelled by the electrostatic force with the positively charged daughter nucleus. But in order to escape, the alpha particle has to tunnel through a potential barrier. See the discussion in Griffiths or elsewhere.

5 Born series and approximation in potential scattering

- Consider the wave mechanical treatment of scattering of non-relativistic particles of mass m against a potential $V(\mathbf{r})$ that vanishes for large $|\mathbf{r}|$. We suppose that free particles (with wave amplitude Ae^{ikz}) come in along the z -axis from $-\infty$ and scatter. Scattered particles are detected at large $r = |\mathbf{r}|$ at the angular location specified by the polar and azimuthal angles θ and ϕ . The scattered wave amplitude is expressed as $f(\theta, \phi)e^{ikr}/r$ for large r . $f(\theta, \phi)$ is called the scattering amplitude. The differential cross section is given by $d\sigma/d\Omega = |f|^2$ and the total cross section is $\sigma = \int |f|^2 d\Omega$ where $d\Omega = \sin\theta d\theta d\phi$ is the element of solid angle. σ with dimensions of area may be thought of as the total effective cross-sectional area (normal to the incident beam) presented by the scattering potential. $d\sigma$ is the average number of particles scattered into the angular region $d\Omega$ per unit time per unit incident flux of particles. The incident flux is $\mathbf{j}_{inc} \cdot \hat{z}$ where \mathbf{j} is the probability current density.

- Max Born’s approximation to find the scattering amplitude $f(\theta, \phi)$ is useful especially when the scattering potential $V(\vec{r})$ is weak compared to the energy of the incoming wave $\hbar^2 k^2/2m$. In such a situation, the scattered wave is expected to be small compared to the incoming plane wave. So it is useful in the regime of high energies while the partial wave approximation is useful at low energies. Loosely, the Born series is an expansion in powers of the potential V , treated as a perturbation to the kinetic term. V need not be spherically symmetric.

5.1 Integral form of the Schrödinger equation and Green’s function for the Helmholtz operator

- The starting point for the Born series is a rewriting of the Schrödinger eigenvalue problem as an integral equation. We begin by writing

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi = \frac{\hbar^2 k^2}{2m}\psi \Rightarrow (\nabla^2 + k^2)\psi = \frac{2mV}{\hbar^2}\psi. \quad (98)$$

$\nabla^2 + k^2$ is the Helmholtz operator and if the rhs $\frac{2mV}{\hbar^2}\psi$ had been a source $\chi(\vec{r})$ independent of $\psi(\vec{r})$, this would be the inhomogeneous Helmholtz equation. Recall that the general solution of an inhomogeneous linear equation $A\psi = \chi$ is given by the sum of a particular solution and the general solution of the homogeneous equation $A\psi = 0$. Though the SE is in fact a homogeneous equation, it pays to think of it as an inhomogeneous Helmholtz equation and treat the rhs $\frac{2mV}{\hbar^2}\psi$ as a small source.

- The idea is to try to invert the operator $\nabla^2 + k^2$ and take it to the rhs. However, $\nabla^2 + k^2$ is not invertible, as it is ‘many to one’, it has zero eigenvalues. Indeed, it has a large null space consisting of all free particle eigenstates: $(\nabla^2 + k^2)\psi_0 = 0$, e.g., the plane waves $\psi_0(\vec{r}) = e^{i\vec{l}\cdot\vec{r}}$ for *any* vector \vec{l} whose length is $|\vec{l}| = k$. These plane waves span the zero eigenspace of the Helmholtz operator (though we could just as well use angular momentum eigenstates of the free particle with energy $\hbar^2 k^2/2m$).

- Though it isn’t invertible, we may be able to find a ‘right inverse’ in the sense of a ‘Green’s function’ $G(r, r')$ satisfying (here ∇ is the gradient in \vec{r} as opposed to the gradient ∇' in \vec{r}')

$$(\nabla^2 + k^2)G(\vec{r}, \vec{r}') = \delta^3(\vec{r} - \vec{r}'). \quad (99)$$

But such a Green’s function is not unique. However, any two Green’s functions $G^{(1)}, G^{(2)}$ for the Helmholtz operator differ by a solution ψ_0 of the homogeneous Helmholtz equation

$$[\nabla^2 + k^2](G^{(1)}(\vec{r}, \vec{r}') - G^{(2)}(\vec{r}, \vec{r}')) = 0 \Rightarrow G^{(1)}(\vec{r}, \vec{r}') - G^{(2)}(\vec{r}, \vec{r}') = \psi_0(r) \quad (100)$$

We will find a Green’s function for the Helmholtz operator shortly. The virtue of having one is that it in effect provides a ‘particular solution’ of the inhomogeneous Helmholtz equation. In more detail, we may write the ‘general solution’ of the SE as

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G(\vec{r}, \vec{r}') \frac{2mV(\vec{r}')}{\hbar^2} \psi(\vec{r}') d^3r' \quad (101)$$

where $\psi_0(\vec{r})$ is any solution of $(\nabla^2 + k^2)\psi = 0$, i.e., a free particle energy eigenstate. It is easily checked that this ψ satisfies the SE. However, it is not an explicit solution since ψ appears both on the left and right sides. Nevertheless, it is an integral equation for ψ which looks a bit

like the scattering boundary condition if we take $\psi_0 = e^{ikz}$! So we should expect the integral expression on the rhs to tend to the scattered wave for large r .

- We can iterate this expression to get the Born series, which gives a formal solution of the SE:

$$\begin{aligned} \psi(r) &= \psi_o(r) + \int G(r, r') \frac{2mV(r')}{\hbar^2} \psi_o(r') dr' + \iint G(r, r') \frac{2mV(r')}{\hbar^2} G(r', r'') \frac{2mV(r'')}{\hbar^2} \psi_o(r'') dr' dr'' \\ &+ \iiint G(r, r') \frac{2mV(r')}{\hbar^2} G(r', r'') \frac{2mV(r'')}{\hbar^2} G(r'', r''') \frac{2mV(r''')}{\hbar^2} \psi_o(r''') dr' dr'' dr''' + \dots \quad (102) \end{aligned}$$

- We still have to find a Green's function for the Helmholtz operator, i.e., any one solution of

$$(\nabla^2 + k^2) G(\vec{r}, \vec{r}') = \delta^3(\vec{r} - \vec{r}'). \quad (103)$$

We will select a solution that is appropriate to the scattering problem. A priori $G(r, r')$ is a function of six coordinates and it is daunting to find a solution of this partial differential equation that involves derivatives in three of them r, θ, ϕ . However, on account of the translation invariance ($\vec{r} \rightarrow \vec{r} + \vec{b}$) of the Helmholtz operator, we choose to look for a Green's function that depends only on the translation-invariant vector $\vec{r} - \vec{r}'$. So we have gone from 6 to 3 variables. Furthermore, on account of the rotation invariance of the Helmholtz operator¹⁰, we choose to look for a Green's function that depends only on the rotation invariant quantity $s = |\vec{s}| = |\vec{r} - \vec{r}'|$. This reduces the above partial differential Helmholtz operator to an ordinary differential operator. $G(s)$ must satisfy¹¹

$$\frac{1}{s} \frac{d^2 s G(s)}{ds^2} + k^2 G(s) = \delta^3(\vec{s}). \quad (104)$$

Let us first consider the case $s > 0$ where this is a homogeneous linear ODE $(sG)'' + k^2 sG = 0$. The general solution is $G(s) = \frac{Ae^{iks}}{s} + \frac{Be^{-iks}}{s}$. However, we choose $B = 0$ since we will be interested in the outgoing scattered wave. To find A , we look at the behavior for small s , where $G(s) \rightarrow \frac{A}{s}$ independent of k . So to find A , it suffices to consider the case $k = 0$. For $k = 0$, it is easy to show that

$$\nabla^2 \left(\frac{1}{r} \right) = -4\pi \delta^3(\vec{r}) \quad (105)$$

For $r \neq 0$, this is immediate since $\nabla^2 r^{-1} = \frac{1}{r} (rr^{-1})'' = 0$. To check that it is correct also at $r = 0$ we integrate over the interior of a unit sphere and use Stokes theorem:

$$\int \vec{\nabla} \cdot \vec{\nabla} \frac{1}{r} d^3r = \int_{S^2} \vec{\nabla} \frac{1}{r} \cdot \hat{r} r^2 d\Omega = \int -\frac{\hat{r}}{r^2} \cdot \hat{r} r^2 d\Omega = -4\pi. \quad (106)$$

¹⁰By rotation-invariance we mean that if $\vec{r}' = (x', y', z') = R\vec{r}$ for a rotation R applied to $\vec{r} = (x, y, z)$, then the formula for the Laplacian $\frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is unchanged. It is good to check this first in two dimensions, where $x' = cx - sy$ and $y' = sx + cy$ for $s = \sin \alpha$ and $c = \cos \alpha$ where α is the angle of (counter-clockwise) rotation. Just as translation-invariance is manifest in Cartesian coordinates, rotation-invariance is manifest in spherical polar coordinates. Suppose the rotation is by a counter-clockwise angle α about some axis. Let us choose our coordinate system so the axis of rotation is the z -axis. Then under such a rotation $(r, \theta, \phi) \mapsto (r, \theta, \phi + \alpha)$. Now the laplacian is $\nabla^2 = \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$. The formula for this differential operator is clearly unchanged under $\phi \rightarrow \phi + \alpha$. Thus the Laplacian is rotation invariant.

¹¹For $G(\vec{r}, \vec{r}') = G(\vec{r} - \vec{r}')$, we can re-cast the derivatives w.r.to \vec{r}' as derivatives with respect to \vec{s} since $\frac{\partial G(x-x')}{\partial x} = \frac{\partial G(x-x')}{\partial(x-x')}$.

So we conclude that $A = -\frac{1}{4\pi}$. Thus we have found one Green's function for the Helmholtz operator

$$G(s) = -\frac{1}{4\pi} \frac{e^{iks}}{s} \quad \text{or} \quad G(\vec{r} - \vec{r}') = -\frac{1}{4\pi} \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r} - \vec{r}'|}. \quad (107)$$

A Green's function is not unique, we can add to this $G(s)$ any solution of the homogeneous equation and get another Green's function. However, for the problem of interest, $G(s)$ is most appropriate, as it satisfies the scattering b.c.

- To summarize, we have written the Schrödinger eigenvalue problem as an integral equation

$$\psi(r) = \psi_0(r) - \frac{1}{4\pi} \int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r} - \vec{r}'|} \frac{2mV(\vec{r}')}{\hbar^2} \psi(\vec{r}') d^3r' \quad (108)$$

and iterated it to obtain the Born series (102).

5.2 Born approximation

So far we have not made any approximation. Now we apply this to the scattering problem by choosing $\psi_0(r) = e^{i\vec{k}\cdot\vec{r}}$ to be the incoming plane wave with $\vec{k} = k\hat{z}$. Notice that successive terms in the Born series involve higher powers of the potential. We suppose that the potential is weak so that the total wave function does not differ much from the incoming plane wave and truncate the Born series after one iteration. This gives the first Born approximation

$$\psi(r) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi} \int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r} - \vec{r}'|} \frac{2mV(\vec{r}')}{\hbar^2} e^{i\vec{k}\cdot\vec{r}'} d^3r' + \mathcal{O}(V^2). \quad (109)$$

To find the scattering amplitude, we must extract the asymptotic behavior for large r and compare with the scattering boundary condition

$$-\frac{1}{4\pi} \int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r} - \vec{r}'|} \frac{2mV(\vec{r}')}{\hbar^2} e^{i\vec{k}\cdot\vec{r}'} d^3r' \rightarrow f(\theta, \phi) \frac{e^{ikr}}{r}. \quad (110)$$

To extract the large r behavior of the integral, we assume that the potential is localized around $\mathbf{r} = 0$, so that the integral over \vec{r}' receives non-trivial contributions only for small r' . So we may assume that $r \gg r'$ inside the integral. The simplest possibility is to take $|\vec{r} - \vec{r}'| \approx r$. Within this crude approximation the scattering amplitude is independent of θ and ϕ (below $\vec{k} = k\hat{z}$ for a plane wave incident from the left)

$$f_{crude}(\theta, \phi) = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \tilde{V}(-\vec{k}) \quad \text{where} \quad \tilde{V}(\vec{k}) = \int V(\vec{r}') e^{-i\vec{k}\cdot\vec{r}'} d^3r'. \quad (111)$$

Though too crude, it indicates that the scattering amplitude is proportional to the Fourier transform of the potential, which we will see is a general feature of the Born approximation.

- To do justice to the first Born approximation and extract the angular dependence of the scattering amplitude, we need a better approximation for $|\vec{r} - \vec{r}'|$. We write

$$|\vec{r} - \vec{r}'|^2 = r^2 - 2\vec{r}\cdot\vec{r}' + r'^2 = r^2 \left(1 - 2\frac{\vec{r}\cdot\vec{r}'}{r^2} + \frac{r'^2}{r^2} \right) \Rightarrow |\vec{r} - \vec{r}'| = r \left(1 - 2\frac{\vec{r}\cdot\vec{r}'}{r^2} + \frac{r'^2}{r^2} \right)^{\frac{1}{2}} = r - \hat{r}\cdot\vec{r}' + \mathcal{O}\left(\frac{r'^2}{r^2}\right).$$

Using $|\vec{r} - \vec{r}'| \approx r - \hat{r} \cdot \vec{r}'$ in the first Born approximation, we get¹²

$$\psi(r) \approx e^{i\vec{k}_i \cdot \hat{r}} - \frac{1}{4\pi} \frac{2m}{\hbar^2} \frac{e^{ikr}}{r} \int V(\vec{r}') e^{-i(\vec{k}_f - \vec{k}_i) \cdot \vec{r}'} d^3r' \quad (112)$$

where we defined $\vec{k}_i = \vec{k}$ for the incoming wave vector and an¹³ outgoing wave vector $\vec{k}_f = k\hat{r}$ in the direction defined by θ, ϕ . From this we can read off the scattering amplitude

$$f(\theta, \phi) = f(\hat{k}_f) = f(\hat{r}) = -\frac{1}{4\pi} \frac{2m}{\hbar^2} \tilde{V}(\vec{k}_f - \vec{k}_i) = -\frac{m}{2\pi\hbar^2} \tilde{V}(\vec{q}). \quad (113)$$

This is the first Born approximation for the scattering amplitude and is valid even if V isn't spherically symmetric. The vector $\vec{q} = \vec{k}_f - \vec{k}_i$ is called the momentum transfer. The main result of the Born approximation is that the scattering amplitude $f(\hat{r})$ is proportional to the Fourier transform of the potential with respect to the momentum transfer $\vec{q} = k\hat{r} - \vec{k}$.

- The Born approximation gives a solution to the direct scattering problem valid at high energies. In treating the potential term in the Hamiltonian $H = \frac{p^2}{2m} + V$ as a perturbation, V has been assumed to be small compared to the free particle energy, which is the energy of the incoming particle in the beam. This is what allows us to replace $\psi(\vec{r}')$ under the integral by the free particle $\psi_0(\vec{r}')$.

- The Born approximation also gives a partial result in inverse scattering: a way to extract the potential if the scattering amplitude is known.

- In the limit of zero momentum transfer $\vec{q} \rightarrow 0$, the Born scattering amplitude simplifies. In this limit, the scattering amplitude is spherically symmetric and sensitive only to the integral of the potential:

$$f_{\vec{q} \rightarrow 0}(\hat{r}) = -\frac{m}{2\pi\hbar^2} \tilde{V}(0) = -\frac{m}{2\pi\hbar^2} \int V(\vec{r}') d^3r'. \quad (114)$$

5.3 Born approximation for spherically symmetric potential

- For a spherically symmetric potential, the Born approximation for the scattering amplitude may be simplified. If $\vec{k} = k\hat{z}$ and $\vec{k}_f = k\hat{r}$, then from the isosceles triangle, the momentum transfer $\vec{q} = \vec{k}_f - \vec{k}_i$ is seen to have a magnitude $q = 2k \sin \frac{\theta}{2}$. To evaluate the Fourier transform of the potential

$$\tilde{V}(\vec{q}) = \int e^{-i\vec{q} \cdot \vec{r}'} V(r') r'^2 dr' \sin \theta' d\theta' d\phi' \quad (115)$$

we pick the \hat{z}' axis to point in the direction of \vec{q} so that $\vec{q} \cdot \vec{r}' = qr' \cos \theta'$ and get

$$\tilde{V}(q) = \int V(r') e^{-iqr' \cos \theta'} r'^2 \sin \theta' dr' d\theta' d\phi' \quad (116)$$

¹²In the denominator we use the crude approximation $|\vec{r} - \vec{r}'| \approx r$. This is because $|\vec{r} - \vec{r}'|^{-1} \approx \frac{1}{r} \left(1 - \frac{\hat{r} \cdot \vec{r}'}{r}\right)^{-1} \approx \frac{1}{r} \left(1 + \frac{\hat{r} \cdot \vec{r}'}{r} + \dots\right) \approx \frac{1}{r} + \frac{\hat{r} \cdot \vec{r}'}{r^2}$. The 2nd term is $\sim r^{-2}$ for $r \rightarrow \infty$ and wouldn't contribute to $f(\theta, \phi)$, which is the coefficient of $\frac{e^{ikr}}{r}$ for large r .

¹³ $\vec{k}_f = k\hat{r}$ is not the wave vector of a plane wave. The outgoing wave is a spherical wave. \hat{k}_f is just a convenient notation for the unit vector \hat{r} in the direction in which we are interested in finding $f(\theta, \phi)$. But it is a reasonable notation, since in an experiment, we would detect a outgoing scattered free particle at angular location θ, ϕ with momentum $\hbar\vec{k}_f$.

We can perform the θ' integral by the substitution $t = \cos \theta'$

$$\int_0^\pi e^{-iqr' \cos \theta'} \sin \theta' d\theta' = \int_{-1}^1 e^{-iqr't} dt = \frac{2 \sin qr'}{qr'} \quad (117)$$

Thus the Fourier transform of a spherically symmetric potential is rotationally invariant in momentum space as well

$$\tilde{V}(\vec{q}) = \tilde{V}(q) = \frac{4\pi}{q} \int_0^\infty V(r') r' \sin qr' dr' \quad (118)$$

Thus the scattering amplitude in the first Born approximation is

$$f(\theta, \phi) = -\frac{2m}{\hbar^2 q} \int_0^\infty V(r) r \sin qr dr \quad \text{where } q = 2k \sin \frac{\theta}{2}. \quad (119)$$

5.4 Rutherford scattering

• In the case of Rutherford scattering of charge q_1 against charge q_2 , the potential is $V(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r}$, and

$$\tilde{V}(q) = \frac{q_1 q_2}{\epsilon_0 q} \int_0^\infty \sin qr dr = \frac{q_1 q_2}{\epsilon_0 q^2} \int_0^\infty \sin \rho d\rho \quad (120)$$

However, the dimensionless oscillatory integral appearing above is not absolutely convergent. In the absence of additional (physical) input we could assign any numerical value to it. However aside from this numerical constant, if we put $q = 2k \sin \theta/2$, we see that the cross section $|\frac{m}{2\pi\hbar^2} \tilde{V}(q)|^2$ resembles the Rutherford cross section. We have already encountered difficulties with the Coulomb potential in that its total scattering cross section is infinite classically. The Coulomb potential does not die off fast enough as $r \rightarrow \infty$ for us to be able to legitimately treat the incoming and scattered particles as free. This is reflected in the above ambiguity in defining the Fourier transform of the Coulomb potential. However, in many physical situations, the Coulomb potential is screened beyond a screening length. So we can treat the Coulomb potential as the $\mu \rightarrow 0$ limit of a screened Coulomb (or Yukawa) potential

$$V(r) = \alpha \frac{e^{-\mu r}}{r} \quad \text{where } \alpha = \frac{q_1 q_2}{4\pi\epsilon_0}. \quad (121)$$

μ^{-1} is called the screening length. For $r > \mu^{-1}$, the Coulomb potential is effectively screened by the exponential damping factor. For the Yukawa potential, we find

$$\tilde{V}(q) = \frac{4\pi}{q} \int_0^\infty \frac{\alpha e^{-\mu r}}{r} r \sin qr dr = \frac{4\pi\alpha}{\mu^2 + q^2}. \quad (122)$$

Putting $\alpha = q_1 q_2 / 4\pi\epsilon_0$ in the limit $\mu \rightarrow 0$ we get for the Coulomb potential

$$\tilde{V}(q) \rightarrow \frac{q_1 q_2}{\epsilon_0} \frac{1}{q^2}. \quad (123)$$

Putting $q = 2k \sin(\theta/2)$ we get the limiting scattering amplitude in the Born approximation

$$f(\theta, \phi) \approx -\frac{2m}{\hbar^2} \frac{q_1 q_2}{4\pi\epsilon_0} \frac{1}{q^2} = -\frac{q_1 q_2}{16\pi\epsilon_0 E} \frac{1}{\sin^2 \theta/2} \quad (124)$$

where $E = \hbar^2 k^2 / 2m$. The differential cross section for Coulomb scattering in the Born approximation is found to match Rutherford's result from classical mechanics

$$\frac{d\sigma}{d\Omega} = |f|^2 \approx \left(\frac{q_1 q_2}{16\pi\epsilon_0 E} \right)^2 \frac{1}{\sin^4 \theta/2}. \quad (125)$$

Scattering in the forward direction dominates, but there is significant scattering through wide angles as well, as found in Rutherford's alpha scattering experiment.