Chapter 7

Approximation methods for stationary states

7.1 Time-independent perturbation theory

While we have succeeded in deriving formal analytical solutions for stationary states of the Schrödinger operator in a variety of settings, in the majority of practical applications, exact solutions are inaccessible.\(^1\) For example, if an atom is placed in an external electric field, the energy levels shift, and the wavefunctions become distorted — the Stark effect. The new energy levels and wavefunctions could in principle be obtained by writing down a complete Hamiltonian, including the external field. Indeed, such a programme may be achieved for the hydrogen atom. But even there, if the external field is small compared with the electric field inside the atom (which is billions of volts per meter) it is easier to compute the changes in the energy levels and wavefunctions within a scheme of successive corrections to the zero-field values. This method, termed perturbation theory, is the single most important method for solving problems in quantum mechanics, and is widely used in atomic physics, condensed matter and particle physics.

\[\text{INFO. It should be acknowledged that there are -- typically very interesting -- problems which cannot be solved using perturbation theory, even when the perturbation is very weak: although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localized potential of strength } \lambda. \text{ As we found earlier in chapter 2, switching on an arbitrarily weak attractive potential causes the } k = 0 \text{ free particle wavefunction to drop below the continuum of plane wave energies and become a localized bound state with binding energy of order } \lambda^2. \text{ However, on changing the sign of } \lambda \text{ to give a repulsive potential, there is no bound state; the lowest energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation cannot be represented as a power series in } \lambda, \text{ the strength of the perturbation. This particular difficulty does not typically occur in three dimensions, where arbitrarily weak potentials do not in general lead to bound states.}\]

\[\text{EXERCISE. Focusing on the problem of bound state formation in one-dimension described above, explore the dependence of the ground state energy on } \lambda. \text{ Consider why a perturbative expansion in } \lambda \text{ is infeasible.}\]

\[^1\text{Indeed, even if such a solution is formally accessible, its complexity may render it of no practical benefit.}\]

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7.1.1 The Perturbation Series

Let us then consider an unperturbed Hamiltonian, $\hat{H}^{(0)}$, having known eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$,

$$\hat{H}^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle .$$

In the following we will address the question of how the eigenstates and eigenenergies are modified by the imposition of a small perturbation, $\hat{H}^{(1)}$ (such as that imposed by an external electric or magnetic field on a charged particle, or the deformation of some other external potential). In short, we are interested in the solution of the Schrödinger equation,

$$\left(\hat{H}^{(0)} + \hat{H}^{(1)}\right)|n\rangle = E_n|n\rangle .$$

If the perturbation is small, $\langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \ll E_n^{(0)}$, it seems natural to suppose that, on turning on $\hat{H}^{(1)}$, the eigenfunctions and eigenvalues will change adiabatically from their unperturbed to their perturbed values, a situation described formally as “adiabatic continuity”,

$$|n^{(0)}\rangle \rightarrow |n\rangle, \quad E_n^{(0)} \rightarrow E_n .$$

However, note that this is not always the case. For example, as mentioned above, an infinitesimal perturbation has the capacity to develop a bound state not present in the unperturbed system. For now, let us proceed with the perturbative expansion and return later to discuss its potential range of validity.

The basic assumption that underpins the perturbation theory is that, for $\hat{H}^{(1)}$ small, the leading corrections are of the same order of magnitude as $\hat{H}^{(1)}$ itself. The perturbed eigenenergies and eigenvalues can then be obtained to a greater accuracy by a successive series of corrections, each of order $\langle \hat{H}^{(1)}\rangle/\langle \hat{H}^{(0)}\rangle$ compared with the previous. To identify terms of the same order in $\langle \hat{H}^{(1)}\rangle/\langle \hat{H}^{(0)}\rangle$, it is convenient to extract from $\hat{H}^{(1)}$ a dimensionless parameter $\lambda$, characterising the relative magnitude of the perturbation against $\hat{H}^{(0)}$, and then expand $|n\rangle$ and $E_n$ as a power series in $\lambda$, i.e.

$$|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots = \sum_{m=0}^{\infty} \lambda^m |n^{(m)}\rangle ,$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots = \sum_{m=0}^{\infty} \lambda^m E_n^{(m)} .$$

One may think of the parameter $\lambda$ as an artificial book-keeping device to organize the perturbative expansion, and which is eventually set to unity at the end of the calculation.

Applied to the stationary form of the Schrödinger equation (7.2), an expansion of this sort leads to the relation

$$\left(\hat{H}^{(0)} + \lambda\hat{H}^{(1)}\right)(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots) .$$

From this equation, we must relate terms of equal order in $\lambda$. At the lowest order, $O(\lambda^0)$, we simply recover the unperturbed equation (7.1). In practical applications, one is usually interested in determining the first non-zero perturbative correction. In the following, we will explore the form of the first and second order perturbative corrections.
7.1.2 First order perturbation theory

Isolating terms from (7.3) which are first order in $\lambda$,
\[ \hat{H}^{(0)}|n^{(1)}\rangle + \hat{H}^{(1)}|n^{(0)}\rangle = E^{(0)}_n|n^{(1)}\rangle + E^{(1)}_n|n^{(0)}\rangle. \]  
and taking the inner product with the unperturbed states $\langle n^{(0)}|$,
one obtains
\[ \langle n^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle + \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle = \langle n^{(0)}|E^{(0)}_n|n^{(1)}\rangle + \langle n^{(0)}|E^{(1)}_n|n^{(0)}\rangle. \]

Noting that $\langle n^{(0)}|\hat{H}^{(0)} = \langle n^{(0)}|E^{(0)}_n$ and exploiting the presumed normalization $\langle n^{(0)}|n^{(0)} \rangle = 1$, one finds that the first order shift in energy is given simply by the expectation value of the perturbation taken with respect to the unperturbed eigenfunctions,
\[ E^{(1)}_n = \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle. \]  

Turning to the wavefunction, if we instead take the inner product of (7.4) with $\langle m^{(0)}|$ (with $m \neq n$), we obtain
\[ \langle m^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle + \langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle = \langle m^{(0)}|E^{(0)}_n|n^{(1)}\rangle + \langle m^{(0)}|E^{(1)}_n|n^{(0)}\rangle. \]

Once again, with $\langle m^{(0)}|\hat{H}^{(0)} = \langle m^{(0)}|E^{(0)}_m$ and the orthogonality condition on the wavefunctions, $\langle m^{(0)}|n^{(0)} \rangle = 0$, one obtains an expression for the first order shift of the wavefunction expressed in the unperturbed basis,
\[ \langle m^{(0)}|n^{(1)}\rangle = \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E^{(0)}_n - E^{(0)}_m}. \]  

In summary, setting $\lambda = 1$, to first order in perturbation theory, we have the eigenvalues and eigenfunctions,
\[ E_n \simeq E^{(0)}_n + \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \]
\[ |n\rangle \simeq |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E^{(0)}_n - E^{(0)}_m}. \]

Before turning to the second order of perturbation theory, let us first consider a simple application of the method.

**Example:** Ground state energy of the Helium atom: For the Helium atom, two electrons are bound to a nucleus of two protons and two neutrons. If one neglects altogether the Coulomb interaction between the electrons, in the ground state, both electrons would occupy the ground state hydrogenic wavefunction (scaled appropriately to accommodate the doubling of the nuclear charge) and have opposite spin. Treating the Coulomb interaction between electrons as a perturbation, one may then use the basis above to estimate the shift in the ground state energy with
\[ \hat{H}^{(1)} = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \]

As we have seen, the hydrogenic wave functions are specified by three quantum numbers, $n$, $\ell$, and $m$. In the ground state, the corresponding wavefunction takes the spatially isotropic form,
\[ \langle \mathbf{r}|n = 1, \ell = 0, m = 0 \rangle = \psi_{100}(\mathbf{r}) = \left( \frac{1}{\pi a^3} \right)^{1/2} e^{-r/a}, \]  

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where \( a = \frac{\alpha e^2}{2\pi \hbar c} \) denotes the atomic Bohr radius for a nuclear charge \( Z \). For the helium atom \((Z = 2)\), the symmetrized ground state of the unperturbed Hamiltonian is then given by the spin singlet \((S = 0)\) electron wavefunction,

\[
|g.s.(0)\rangle = \frac{1}{\sqrt{2}} \left( |100, \uparrow \rangle \otimes |100, \downarrow \rangle - |100, \downarrow \rangle \otimes |100, \uparrow \rangle \right).
\]

Here we have used the direct product \( \otimes \) to discriminate between the two electrons. Then, applying the perturbation theory formula above (7.5), to first order in the Coulomb interaction, the energy shift is given by

\[
E_n^{(1)} = \langle g.s.(0) | \hat{H}^{(1)} | g.s.(0) \rangle = \frac{e^2}{4\pi \varepsilon_0} \frac{1}{\alpha^3} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^{-2|\mathbf{r}_1 + \mathbf{r}_2|/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{e^2}{4\pi \varepsilon_0} \frac{C_0}{2a},
\]

where we have defined the dimensionless constant \( C_0 = \frac{1}{(4\pi)^2} \int d\mathbf{z}_1 d\mathbf{z}_2 e^{-\alpha|\mathbf{z}_1 - \mathbf{z}_2|} \). Then, making use of the identity,

\[
\frac{1}{(4\pi)^2} \int d\Omega_1 d\Omega_2 \frac{1}{|\mathbf{z}_1 - \mathbf{z}_2|} = \frac{1}{\max(z_1, z_2)},
\]

where the integrations runs over the angular coordinates of the vectors \( \mathbf{z}_1 \) and \( \mathbf{z}_2 \), and \( z_1, z_2 = |\mathbf{z}_1|, |\mathbf{z}_2| \), one finds that \( C_0 = 2 \int_0^\infty dz_1 z_1^2 e^{-z_1} \int_0^\infty dz_2 z_2^2 e^{-z_2} = 5/4 \). As a result, noting that the Rydberg energy, \( \text{Ry} = \frac{2\pi^2}{4\alpha \varepsilon_0} \), we obtain the first order energy shift \( \Delta E = \frac{1}{2} \zeta Z \text{Ry} \simeq 34 \text{eV} \) for \( Z = 2 \). This leads to a total ground state energy of \((2Z^2 - \frac{1}{2} \zeta) \text{Ry} \) \(-5.5 \text{Ry} \simeq -74.8 \text{eV} \) compared to the experimental value of \(-5.807 \text{Ry} \).

### 7.1.3 Second order perturbation theory

With the first order of perturbation theory in place, we now turn to consider the influence of the second order terms in the perturbative expansion (7.3). Isolating terms of order \( \lambda^2 \), we have

\[
\hat{H}^{(0)}|n(2)\rangle + \hat{H}^{(1)}|n(1)\rangle = E^{(1)}_n|n(1)\rangle + E^{(2)}_n|n(0)\rangle.
\]

As before, taking the inner product with \( \langle n(0) | \), one obtains

\[
\langle n(0) | \hat{H}^{(0)}|n(2)\rangle + \langle n(0) | \hat{H}^{(1)}|n(1)\rangle = \langle n(0) | E^{(1)}_n|n(1)\rangle + \langle n(0) | E^{(2)}_n|n(0)\rangle.
\]

Noting that the first two terms on the left and right hand sides cancel, we are left with the result

\[
E^{(2)}_n = \langle n(0) | \hat{H}^{(1)}|n(1)\rangle - E^{(1)}_n \langle n(0) | n(1)\rangle.
\]

Previously, we have made use of the normalization of the basis states, \( |n(0)\rangle \). We have said nothing so far about the normalization of the exact eigenstates, \( |n\rangle \). Of course, eventually, we would like to ensure normalization of these states too. However, to facilitate the perturbative expansion, it is operationally more convenient to impose a normalization on \( |n\rangle \) through the condition \( \langle n(0) | n \rangle = 1 \). Substituting the \( \lambda \) expansion for \( |n\rangle \), we thus have

\[
\langle n(0) | n \rangle = 1 = \langle n(0) | n(0) \rangle + \lambda \langle n(0) | n(1) \rangle + \lambda^2 \langle n(0) | n(2) \rangle + \cdots.
\]

From this relation, it follows that \( \langle n(0) | n(1) \rangle = \langle n(0) | n(2) \rangle = \cdots = 0 \).\(^2\) We can therefore drop the term \( E^{(1)}_n \langle n(0) | n(1)\rangle \) from consideration. As a result, we

\(^2\)Alternatively, would we suppose that \( |n\rangle \) and \( |n(0)\rangle \) were both normalised to unity, to leading order, \( |n\rangle = |n(0)\rangle + |n(1)\rangle \), and \( \langle n(0) | n(1) \rangle + \langle n(1) | n(0) \rangle = 0 \), i.e. \( \langle n(0) | n(1) \rangle \) is pure imaginary. This means that if, to first order, \( |n\rangle \) has a component parallel to \( |n(0)\rangle \), that component has a small imaginary amplitude allowing us to define \( |n\rangle = e^{i\phi}|n(0)\rangle \) + orthog. components. However, the corresponding phase factor \( \phi \) can be eliminated by redefining the phase of \( |n\rangle \). Once again, we can conclude that the term \( E^{(1)}_n \langle n(0) | n(1)\rangle \) can be eliminated from consideration.

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obtain
\[ E_n^{(2)} = \langle n^{(0)} | \hat{H}^{(1)} | n^{(1)} \rangle = \langle n^{(0)} | \hat{H}^{(1)} \sum_{m \neq n} | n^{(0)} \rangle \frac{\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} , \]
i.e.
\[ E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} . \tag{7.8} \]

From this result, we can conclude that,

- for the ground state, the second order shift in energy is always negative;
- if the matrix elements of \( \hat{H}^{(1)} \) are of comparable magnitude, neighbouring levels make a larger contribution than distant levels;
- Levels that lie in close proximity tend to be repelled;
- If a fraction of the states belong to a continuum, the sum in Eq. (7.8) should be replaced by an integral.

Once again, to illustrate the utility of the perturbative expansion, let us consider a concrete physical example.

**Example: The Quadratic Stark Effect**: Consider the influence of an external electric field on the ground state of the hydrogen atom. As the composite electron and proton are drawn in different directions by the field, the relative displacement of the electron cloud and nucleus results in the formation of a dipole which serves to lower the overall energy. In this case, the perturbation due to the external field takes the form
\[ \hat{H}^{(1)} = q Ez = q E \cos \theta , \]
where \( q = -|e| \) denotes the electron charge, and the electric field, \( E = E \hat{e}_z \) is oriented along the \( z \)-axis. With the non-perturbed energy spectrum given by \( E_{nlm}^{(0)} \equiv E_n^{(0)} = -\text{Ry}/n^2 \), the ground state energy is given by \( E^{(0)} \equiv E_{100}^{(0)} = -\text{Ry} \). At first order in the electric field strength, \( E \), the shift in the ground state energy is given by \( E^{(1)} = \langle 100 | q E z | 100 \rangle \) where the ground state wavefunction was defined above (7.7). Since the potential perturbation is antisymmetric in \( z \), it is easy to see that the energy shift vanishes at this order.

We are therefore led to consider the contribution second order in the field strength. Making use of Eq. (7.8), and neglecting the contribution to the energy shift from the continuum of unbound positive energy states, we have
\[ E^{(2)} = \sum_{n' \neq 1, l,m} \frac{|\langle nlm | e Ez | 100 \rangle|^2}{E_{1}^{(0)} - E_{n'}^{(0)}} , \]
where \( |nlm\rangle \) denote the set of bound state hydrogenic wavefunctions. Although the expression for \( E^{(2)} \) can be computed exactly, the programme is somewhat tedious. However, we can place a strong bound on the energy shift through the following argument: Since, for \( n > 2 \), \( |E_n^{(0)} - E_{n'}^{(0)}| > |E_1^{(0)} - E_2^{(0)}| \), we have
\[ |E^{(2)}| < \frac{1}{E_{2}^{(0)} - E_{1}^{(0)}} \sum_{n' \neq 1, l,m} \langle 100 | e Ez | nlm \rangle \langle nlm | e Ez | 100 \rangle . \]
Since \( \sum_{n' \neq 1, l,m} |nlm\rangle \langle nlm| = \mathbb{1} \), we have \( \sum_{n' \neq 1, l,m} |nlm\rangle \langle nlm| = \mathbb{1} - |100\rangle \langle 100| \). Finally, since \( \langle 100 | z | 100 \rangle = 0 \), we can conclude that \( |E^{(2)}| < \frac{1}{E_{2}^{(0)} - E_{1}^{(0)}} \langle 100 | e Ez | 100 \rangle^2 |100\rangle . \) With \( \langle 100 | z^2 | 100 \rangle = a_0^2, E_{1}^{(0)} = -\frac{\epsilon^2}{4\pi \epsilon_0 2a_0} = -\text{Ry}, \) and \( E_{2}^{(0)} = E_{1}^{(0)}/4 \), we have
\[ |E^{(2)}| < \frac{1}{4\epsilon^2/8\pi \epsilon_0 a_0} (eE)^2 a_0^2 = \frac{8}{3} 4\pi \epsilon_0 E^2 a_0^3 . \]
Furthermore, since all terms in the perturbation series for $E^{(2)}$ are negative, the first term in the series sets a lower bound, $|E^{(2)}| > |E^{(0)}|$, so we can show that $0.55 \times \frac{8}{9} 4 \pi \alpha |E^{(2)}| < |E^{(2)}| < \frac{4}{9} \pi \alpha |E^{(2)}|$. From this result, one can show that $0.55 \times \frac{8}{9} 4 \pi \alpha |E^{(2)}| < |E^{(2)}| < \frac{4}{9} \pi \alpha |E^{(2)}|$ (exercise).\(^3\)

7.2 Degenerate perturbation theory

The perturbative analysis above is reliable providing that the successive terms in the expansion form a convergent series. A necessary condition is that the matrix elements of the perturbing Hamiltonian must be smaller than the corresponding energy level differences of the original Hamiltonian. If it has different states with the same energy (i.e., degeneracies), and the perturbation has non-zero matrix elements between these degenerate levels, then obviously the theory breaks down. However, the problem is easily fixed. To understand how, let us consider a particular example.

Recall that, for the simple harmonic oscillator, $\hat{H} = \frac{x^2}{2m} + \frac{1}{2}m\omega^2x^2$, the ground state wavefunction is given by $\langle x|0\rangle = (\frac{m\omega}{\pi \hbar})^{1/2} e^{-\xi^2/2}$, where $\xi = x\sqrt{m\omega/\hbar}$ and the first excited state by $\langle x|1\rangle = (\frac{m\omega}{\pi \hbar})^{1/2} e^{-\xi^2/2}$. The wavefunctions for the two-dimensional harmonic oscillator,

$$\hat{H}^{(0)} = \frac{1}{2m}(p_x^2 + p_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2),$$

are given simply by the product of two one-dimensional oscillators. So, setting $\eta = y\sqrt{m\omega/\hbar}$, the ground state is given by $\langle x, y|0, 0\rangle = (\frac{m\omega}{\pi \hbar})^{1/2} e^{-\xi^2 + \eta^2}/2$, and the two degenerate first excited states, an energy $\hbar\omega$ above the ground state, are given by,

$$\langle x, y|1, 0\rangle = (\frac{m\omega}{\pi \hbar})^{1/2} e^{-\xi^2 + \eta^2/2} \langle \xi \eta \rangle.$$

Suppose now we add to the Hamiltonian a perturbation,

$$\hat{H}^{(1)} = \alpha m\omega x y = \alpha \hbar \omega \xi \eta,$$

controlled by a small parameter $\alpha$. Notice that, by symmetry, the following matrix elements all vanish, $\langle 0, 0|\hat{H}^{(1)}|0, 0\rangle = \langle 1, 0|\hat{H}^{(1)}|1, 0\rangle = \langle 0, 1|\hat{H}^{(1)}|0, 1\rangle = \langle 1, 1|\hat{H}^{(1)}|1, 1\rangle = 0$. Therefore, according to a naive perturbation theory, there is no first-order correction to the energies of these states. However, on proceeding to consider the second-order correction to the energy, the theory breaks down. The off-diagonal matrix element, $\langle 1, 0|\hat{H}^{(1)}|0, 1\rangle = 0$ is non-zero, but the two states $|0, 1\rangle$ and $|1, 0\rangle$ have the same energy! This gives an infinite term in the series for $E^{(2)}$.

Yet we know that a small perturbation of this type will not wreck a two-dimensional simple harmonic oscillator – so what is wrong with our approach? To understand the origin of the problem and its fix, it is helpful to plot the original harmonic oscillator potential $\frac{1}{2}m\omega^2(x^2 + y^2)$ together with the perturbing potential $\alpha m\omega x y$. The first of course has circular symmetry, the second has two symmetry axes oriented in the directions $x = \pm y$, climbing most steeply from the origin along $x = y$, falling most rapidly in the directions $x = y$. If we combine the two potentials into a single quadratic form,

$$\frac{1}{2}m\omega^2(x^2 + y^2) + \alpha m\omega x y = \frac{1}{2}m\omega^2 \left[ (1 + \alpha) \left( \frac{x + y}{\sqrt{2}} \right)^2 + (1 - \alpha) \left( \frac{x - y}{\sqrt{2}} \right)^2 \right].$$

\(^3\)Energetic readers might like to contemplate how the exact answer of $|E^{(2)}| = \frac{2}{3} \omega^2 a_0^2$ can be found exactly. The method can be found in the text by Shankar.

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the original circles of constant potential become ellipses, with their axes aligned along \( x = \pm y \).

As soon as the perturbation is introduced, the eigenstates lie in the direction of the new elliptic axes. This is a large change from the original \( x \) and \( y \) bases, which is not proportional to the small parameter \( \alpha \). But the original unperturbed problem had circular symmetry, and there was no particular reason to choose the \( x \) and \( y \) axes as we did. If we had instead chosen as our original axes the lines \( x = \pm y \), the basis states would not have undergone large changes on switching on the perturbation. The resolution of the problem is now clear: Before switching on the perturbation, one must choose a set of basis states in a degenerate subspace in which the perturbation is diagonal.

In fact, for the simple harmonic oscillator example above, the problem can of course be solved exactly by rearranging the coordinates to lie along the symmetry axes, \( (x \pm y)/\sqrt{2} \). It is then clear that, despite the results of naïve first order perturbation theory, there is indeed a first order shift in the energy levels, \( \hbar \omega \rightarrow \hbar \omega \sqrt{1 \pm \alpha} \approx \hbar \omega (1 \pm \alpha/2) \).

\[ \begin{bmatrix} \psi_{200}(r) \\ \psi_{210}(r) \\ \psi_{21 \pm 1}(r) \end{bmatrix} = \left( \frac{1}{32\pi a_0^6} \right)^{1/2} e^{-r/2a_0} \begin{bmatrix} \left( 2 - \frac{r}{a_0} \right) e^{\pm i \alpha / 2} \\ \frac{r}{a_0} \cos \theta e^{\pm i \alpha / 2} \\ \frac{r}{a_0} \sin \theta e^{\pm i \alpha / 2} \end{bmatrix} . \]

When perturbing this system with an electric field oriented in the \( z \)-direction, \( \hat{H}^{(1)} = qE \cos \theta \), a naïve application of perturbation theory predicts no first-order shift in any of these energy levels. However, at second order in \( E \), there is a non-zero matrix element between two degenerate levels \( \Delta = \langle 200 | \hat{H}^{(1)} | 210 \rangle \). All the other matrix elements between these basis states in the four-dimensional degenerate subspace are zero. So the only diagonalization necessary is within the two-dimensional degenerate subspace spanned by \([200]\) and \([210]\), i.e.

\[ \hat{H}^{(1)} = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} , \]

with \( \Delta = qE \left( \frac{1}{32\pi a_0^6} \right) \int \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/2a_0} r^2 \sin \theta \, dr \, d\theta \, d\phi = -3qEa_0 \).

Diagonalizing \( \hat{H}^{(1)} \) within this sub-space, the new basis states are given by the symmetric and antisymmetric combinations, \( \langle 200 \pm | 210 \rangle / \sqrt{2} \) with energy shifts \( \pm \Delta, \) linear in the perturbing electric field. The states \( 2(\ell, \pm 1) \) are not changed by the presence of the field to this level of approximation, so the complete energy map of the \( n = 2 \) states in the electric field has two states at the original energy of \(-\text{Ry}/4\), one state moved up from that energy by \( \Delta \), and one down by \( \Delta \). Notice that the new eigenstates \( \langle 200 \pm | 210 \rangle / \sqrt{2} \) are not eigenstates of the parity operator -- a sketch of their wavefunctions reveals that, in fact, they have non-vanishing electric dipole moment \( \mu \). Indeed this is the reason for the energy shift, \( \pm \Delta = \mp 2\pi eEa_0 = \mp \mu \cdot E \).

\[ \begin{bmatrix} \psi_{200}(r) \\ \psi_{210}(r) \\ \psi_{21 \pm 1}(r) \end{bmatrix} = \left( \frac{1}{32\pi a_0^6} \right)^{1/2} e^{-r/2a_0} \begin{bmatrix} \left( 2 - \frac{r}{a_0} \right) e^{\pm i \alpha / 2} \\ \frac{r}{a_0} \cos \theta e^{\pm i \alpha / 2} \\ \frac{r}{a_0} \sin \theta e^{\pm i \alpha / 2} \end{bmatrix} . \]

\[ \begin{bmatrix} H^{(1)} \end{bmatrix} = \begin{bmatrix} 0 & \Delta \\ \Delta & 0 \end{bmatrix} , \]

with \( \Delta = qE \left( \frac{1}{32\pi a_0^6} \right) \int \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/2a_0} r^2 \sin \theta \, dr \, d\theta \, d\phi = -3qEa_0 \).

Diagonalizing \( H^{(1)} \) within this sub-space, the new basis states are given by the symmetric and antisymmetric combinations, \( \langle 200 \pm | 210 \rangle / \sqrt{2} \) with energy shifts \( \pm \Delta, \) linear in the perturbing electric field. The states \( 2(\ell, \pm 1) \) are not changed by the presence of the field to this level of approximation, so the complete energy map of the \( n = 2 \) states in the electric field has two states at the original energy of \(-\text{Ry}/4\), one state moved up from that energy by \( \Delta \), and one down by \( \Delta \). Notice that the new eigenstates \( \langle 200 \pm | 210 \rangle / \sqrt{2} \) are not eigenstates of the parity operator -- a sketch of their wavefunctions reveals that, in fact, they have non-vanishing electric dipole moment \( \mu \). Indeed this is the reason for the energy shift, \( \pm \Delta = \mp 2\pi eEa_0 = \mp \mu \cdot E \).

**Example:** Linear Stark Effect: As with the two-dimensional harmonic oscillator discussed above, the hydrogen atom has a non-degenerate ground state, but degeneracy in its lowest excited states. Specifically, there are four \( n = 2 \) states, all having energy \(-\frac{1}{4}\) Ry. In spherical coordinates, these wavefunctions are given by

\[
\begin{bmatrix} \psi_{200}(r) \\ \psi_{210}(r) \\ \psi_{21 \pm 1}(r) \end{bmatrix} = \left( \frac{1}{32\pi a_0^6} \right)^{1/2} e^{-r/2a_0} \begin{bmatrix} \left( 2 - \frac{r}{a_0} \right) e^{\pm i \alpha / 2} \\ \frac{r}{a_0} \cos \theta e^{\pm i \alpha / 2} \\ \frac{r}{a_0} \sin \theta e^{\pm i \alpha / 2} \end{bmatrix} .
\]

When perturbing this system with an electric field oriented in the \( z \)-direction, \( \hat{H}^{(1)} = qE \cos \theta \), a naïve application of perturbation theory predicts no first-order shift in any of these energy levels. However, at second order in \( E \), there is a non-zero matrix element between two degenerate levels \( \Delta = \langle 200 | \hat{H}^{(1)} | 210 \rangle \). All the other matrix elements between these basis states in the four-dimensional degenerate subspace are zero. So the only diagonalization necessary is within the two-dimensional degenerate subspace spanned by \([200]\) and \([210]\), i.e.

\[ \hat{H}^{(1)} = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix} , \]

with \( \Delta = qE \left( \frac{1}{32\pi a_0^6} \right) \int \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/2a_0} r^2 \sin \theta \, dr \, d\theta \, d\phi = -3qEa_0 \).

Diagonalizing \( \hat{H}^{(1)} \) within this sub-space, the new basis states are given by the symmetric and antisymmetric combinations, \( \langle 200 \pm | 210 \rangle / \sqrt{2} \) with energy shifts \( \pm \Delta, \) linear in the perturbing electric field. The states \( 2(\ell, \pm 1) \) are not changed by the presence of the field to this level of approximation, so the complete energy map of the \( n = 2 \) states in the electric field has two states at the original energy of \(-\text{Ry}/4\), one state moved up from that energy by \( \Delta \), and one down by \( \Delta \). Notice that the new eigenstates \( \langle 200 \pm | 210 \rangle / \sqrt{2} \) are not eigenstates of the parity operator -- a sketch of their wavefunctions reveals that, in fact, they have non-vanishing electric dipole moment \( \mu \). Indeed this is the reason for the energy shift, \( \pm \Delta = \mp 2\pi eEa_0 = \mp \mu \cdot E \).

**Example:** As a second and important example of the degenerate perturbation theory, let us consider the problem of a particle moving in one dimension and subject to a weak periodic potential, \( V(x) = 2V \cos(2\pi x/a) \) -- the nearly free electron model. This problem provides a caricature of a simple crystalline solid in which (free) conduction electrons propagate in the presence of a periodic background lattice potential. Here we suppose that the strength of the potential \( V \) is small as compared to the typical energy scale of the particle so that it may be treated as a small pertur-
bation. In the following, we will suppose that the total one-dimensional system is of length $L = Na$, with periodic boundary conditions.

For the unperturbed free particle system, the eigenstates are simply plane waves $\psi_k(x) = (x|k) = \frac{1}{\sqrt{L}} e^{ikx}$ indexed by the wavenumber $k = 2\pi n/L$, $n$ integer, and the unperturbed spectrum is given by $E_k^{(0)} = \hbar^2 k^2/2m$. The matrix elements of the perturbation between states of different wavevector are given by

$$\langle k'|V|k \rangle = \frac{1}{L} \int_0^L dx e^{i(k'-k)x} 2V \cos(2\pi x/a)$$

$$= \frac{V}{L} \int_0^L dx \left( e^{i(k'-k+2\pi/a)x} + e^{i(k'-k-2\pi/a)x} \right) = V \delta_{k'-k, \pm 2\pi/a}.$$

Note that all diagonal matrix elements of the perturbation are identically zero. In general, for wavevectors $k$ and $k'$ separated by $G = 2\pi/a$, the unperturbed states are non-degenerate. For these states one can compute the relative energy shift within the framework of second order perturbation theory. However, for states $k = -k' = G/2 \equiv \pi/a$, the unperturbed free particle spectrum is degenerate. Here, and in the neighbourhood of these $k$ values, we must implement a degenerate perturbation theory.

For the sinusoidal potential considered here, only states separated by $G = 2\pi/a$ are coupled by the perturbation. We may therefore consider matrix elements of the full Hamiltonian between pairs of coupled states, $|k = G/2 + q\rangle$ and $|k = -G/2 + q\rangle$

$$H = \begin{pmatrix} E_{G/2+q}^{(0)} & V \\ V & E_{-G/2+q}^{(0)} \end{pmatrix}.$$

As a result, to leading order in $V$, we obtain the eigenvalues,

$$E_q = \frac{\hbar^2}{2m} \left( q^2 + (\pi/a)^2 \right) \pm \left( V^2 + \frac{\pi^2 \hbar^4 q^2}{4m^2a^2} \right)^{1/2}.$$

In particular, this result shows that, for $k = \pm G/2$, the degeneracy of the free particle system is lifted by the potential. In the vicinity, $|q| \ll G$, the spectrum of eigenvalues is separated by a gap of size $2V$. The appearance of the gap mirrors the behaviour found in our study of the Kronig-Penney model of a crystal studied in section 2.2.3.

The appearance of the gap has important consequences in theory of solids. Electrons are fermions and have to obey Pauli’s exclusion principle. In a metal, at low temperatures, electrons occupy the free particle-like states up to some (Fermi) energy which lies away from gap. Here, the accessibility of very low-energy excitations due to the continuum of nearby states allows current to flow when a small electric field is applied. However, when the Fermi energy lies in the gap created by the lattice potential, an electric field is unable to create excitations and induce current flow. Such systems are described as (band) insulators.

### 7.3 Variational method

So far, in devising approximation methods for quantum mechanics, we have focused on the development of a perturbative expansion scheme in which the states of the non-perturbed system provided a suitable platform. Here, by suitable, we refer to situations in which the states of the unperturbed system mirror those of the full system – adiabatic contunity. For example, the states of the harmonic oscillator potential with a small perturbation will mirror those of the unperturbed Hamiltonian: The ground state will be nodeless, the first excited state will be antisymmetric having one node, and so on. However, often we working with systems where the true eigenstates of the problem may not be adiabatically connected to some simple unperturbed reference state. This
situation is particularly significant in strongly interacting quantum systems where many-particle correlations can effect phase transitions to new states of matter – e.g. the development of superfluid condensates, or the fractional quantum Hall fluid. To address such systems if it is often extremely effective to “guess” and then optimize a trial wavefunction. The method of optimization relies upon a simple theoretical framework known as the variational approach. For reasons that will become clear, the variational method is particularly well-suited to addressing the ground state.

The variational method involves the optimization of some trial wavefunction on the basis of one or more adjustable parameters. The optimization is achieved by minimizing the expectation value of the energy on the trial function, and thereby finding the best approximation to the true ground state wave function. This seemingly crude approach can, in fact, give a surprisingly good approximation to the ground state energy but, it is usually not so good for the wavefunction, as will become clear. However, as mentioned above, the real strength of the variational method arises in the study of many-body quantum systems, where states are more strongly constrained by fundamental symmetries such as “exclusion statistics”.

To develop the method, we’ll begin with the problem of a single quantum particle confined to a potential, \( \hat{H} = \frac{\hat{p}^2}{2m} + V(r) \). If the particle is restricted to one dimension, and we’re looking for the ground state in any fairly localized potential well, it makes sense to start with a trial wavefunction which belongs to the family of normalized Gaussians, \( |\psi(\alpha)\rangle = (\alpha/\pi)^{1/4}e^{-\alpha x^2}/2 \). Such a trial state fulfills the criterion of being nodeless, and is exponentially localized to the region of the binding potential. It also has the feature that it includes the exact ground states of the harmonic binding potential.

The variation approach involves simply minimizing the expectation value of the energy, \( E = \langle \psi(\alpha) | \hat{H} | \psi(\alpha) \rangle \), with respect to variations of the variational parameter, \( \alpha \). (Of course, as with any minimization, one must check that the variation does not lead to a maximum of the energy!) Not surprisingly, this programme leads to the exact ground state for the simple harmonic oscillator potential, while it serves only as an approximation for other potentials. What is perhaps surprising is that the result is only off by only ca. 30% or so for the attractive \( \delta \)-function potential, even though the wavefunction looks substantially different. Obviously, the Gaussian family cannot be used if there is an infinite wall anywhere: one must find a family of wavefunctions vanishing at such a boundary.

\( \blacktriangleright \) Exercise. Using the Gaussian trial state, find the optimal value of the variational state energy, \( E \), for an attractive \( \delta \)-function potential and compare it with the exact result.

To gain some further insight into the approach, suppose the Hamiltonian \( \hat{H} \) has a set of eigenstates, \( \hat{H}|n\rangle = E_n|n\rangle \). Since the Hamiltonian is Hermitian, these states span the space of possible wave functions, including our variational family of Gaussians, so we can write, \( |\psi(\alpha)\rangle = \sum_n a_n(\alpha)|n\rangle \). From this expansion, we have

\[
\frac{\langle \psi(\alpha) | \hat{H} | \psi(\alpha) \rangle}{\langle \psi(\alpha) | \psi(\alpha) \rangle} = \sum_n |a_n|^2 E_n \geq E_0.
\]

for any \( |\psi(\alpha)\rangle \). (We don’t need the denominator if we’ve chosen a family of normalized wavefunctions, as we did with the Gaussians above.) Evidently,
minimizing the left hand side of this equation as function of $\alpha$ provides an upper bound on the ground state energy.

We can see immediately that this will probably be better for finding the ground state energy than for the wavefunction: Suppose the optimum state in our family is given by, say, $|\alpha_{\text{min}}\rangle = N(|0\rangle + 0.2|1\rangle)$ with the normalization $N \simeq 0.98$, i.e. a $20\%$ admixture of the first excited state. Then the wavefunction is off by ca. $20\%$, but the energy estimate will be too high by only $0.04(E_1 - E_0)$, usually a much smaller error.

\textbf{Example:} To get some idea of of how well the variational approach works, consider its application to the to the ground state of the hydrogen atom. Taking into account the spherical symmetry of the ground state, we may focus on the one-dimensional radial component of the wavefunction. Defining the trial radial wavefunction $u(\rho)$, where $\rho = r/a_0$, the variational energy is given by

$$E(u) = -\text{Ry} \frac{\int_0^\infty d\rho \, u(\rho) \left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\right) u(\rho)}{\int_0^\infty d\rho \, u^2(\rho)}.$$ 

For the three families of trial functions,

$$u_1(\rho) = \rho e^{-\alpha\rho}, \quad u_2(\rho) = \frac{\rho}{\alpha^2 + \rho^2}, \quad u_3(\rho) = \rho^2 e^{-\alpha\rho},$$

and finds $\alpha_{\text{min}} = 1, \pi/4, \text{and } 3/2$ respectively (exercise). The first family, $u_1$, includes the exact result, and the minimization procedure correctly finds it. For the three families, the predicted energy of the optimal state is off by $0, 25\%$, and $21\%$ respectively.

The corresponding error in the wavefunction is defined by how far the square of the overlap with the true ground state wavefunction falls short of unity. For the three families, $\varepsilon = 1 - |\langle \psi_0 | \psi_{\text{val}} \rangle|^2 = 0, 0.21, \text{and } 0.05$. Notice here that our handwaving argument that the energies would be found much more accurately than the wavefunctions seems to come unstuck. The third family has far better wavefunction overlap than the second, but only a slightly better energy estimate. Why? A key point is that the potential is singular at the origin; there is a big contribution to the potential energy from a rather small region, and the third family of trial states is the least accurate of the three there. The second family of functions are very inaccurate at large distances: the expectation value $\langle r \rangle = 1.5a_0, \infty, 1.66a_0$ for the three families. But at large distances, both kinetic and potential energies are small, so the result can still look reasonable. These examples reinforce the point that the variational method should be implemented with some caution.

In some cases, one can exploit symmetry to address the properties of higher-lying states. For example, if the one-dimensional attractive potential is symmetric about the origin, and has more than one bound state, the ground state will be even, the first excited state odd. Therefore, we can estimate the energy of the first excited state by minimizing a family of odd functions, such as $\psi(x, \alpha) = (\frac{\sqrt{\pi}}{2a_0^{3/2}})^{1/2} xe^{-\alpha x^2/2}$.

\textbf{Example: Helium atom addressed by the variational approach:} For the hydrogen atom, we know that the ground state energy is $1 \text{ Ry, or } 13.6 \text{ eV}$. The He\textsuperscript{+} ion (with just a single electron) has a nuclear charge of $Z = 2$, so the ground state energy of the electron, being proportional to $Z^2$, will now be equal to $4 \text{ Ry}$. Therefore, for the He atom, if we neglect their mutual interaction, the electrons will occupy the ground state wavefunction having opposite spin, leading to a total ground state energy of $8 \text{ Ry or } 109 \text{ eV}$. In practice, as we have seen earlier, the repulsion between the electrons lowers ground state energy to $79 \text{ eV}$ (see page 64).

To get a better estimate for the ground state energy, one can retain the form of the ionic wavefunction, $(\frac{2}{\pi a_0^3})^{1/2} e^{-Zr/a_0}$, but rather than setting the nuclear charge...
7.4. WENTZEL, KRAMERS AND BRILLOUIN (WKB) METHOD

$Z = 2$, leave it as a variational parameter. In other words, let us accommodate the effects of electron-electron repulsion, which must “push” the wavefunctions to larger radii, by keeping exactly the same wavefunction profile but lessening the effective nuclear charge as reflected in the spread of the wavefunction from $Z = 2$ to $Z < 2$. The precise value will be set by varying it to find the minimum total energy, including the term from electron-electron repulsion.

To find the potential energy from the nuclear-electron interactions, we of course must use the actual nuclear charge $Z = 2$, but impose a variable $Z$ for the wavefunction, so the nuclear potential energy for the two electrons is given by,

$$p.e. = -2 \times \frac{2e^2}{4\pi\epsilon_0} \int_0^\infty 4\pi r^2 dr \frac{Z^3 Z^2 / a_0}{r} e^{-2Zr/a_0} = -Z \frac{e^2}{\pi\epsilon_0 a_0} = -8Z \text{ Ry.}$$

This could have been inferred from the formula for the one electron ion, where the potential energy for the one electron is $-2Z^2 \text{ Ry}$, one factor of $Z$ being from the nuclear charge, the other from the consequent shrinking of the orbit. The kinetic energy is even easier to determine: it depends entirely on the form of the wavefunction, and not on the actual nuclear charge. So for our trial wavefunction it has to be $Z^2 \text{ Ry}$ per electron. Finally, making use of our calculation on page 64, we can immediately write down the positive contribution to the energy expectation value from the electron-electron interaction,

$$\frac{e^2}{4\pi\epsilon_0} \frac{Z^3}{(\pi a_0^2)^2} \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-2Z(r_1 + r_2)/a_0} = \frac{5}{4} \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{5}{4} Z \text{ Ry.}$$

Collecting all of the terms, the total variational state energy is given by:

$$E = -2 \left( 4Z - Z^2 - \frac{5}{8} Z \right) \text{ Ry.}$$

Minimization of this energy with respect to $Z$ obtains the minimum at $Z = 2 - \frac{5}{16}$, leading to an energy of 77.5 eV. This result departs from the true value by about 1 eV. So, indeed, the presence of the other electron leads effectively to a shielding of the nuclear charge by an amount of ca. $\frac{5}{16} e$.

This completes our discussion of the principles of the variational approach. However, later in the course, we will find the variational methods appearing in several important applications. Finally, to close this section on approximation methods for stationary states, we turn now to consider a framework which makes explicit the connection between the quantum and classical theory in the limit $\hbar \to 0$.

7.4 Wentzel, Kramers and Brillouin (WKB) method

The WKB (or Wentzel, Kramers and Brillouin) approximation describes a “quasi-classical” method for solving the one-dimensional time-independent Schrödinger equation. Note that the consideration of one-dimensional systems is less restrictive that it may sound as many symmetrical higher-dimensional problems are rendered effectively one-dimensional (e.g. the radial equation for the hydrogen atom). The WKB method is named after physicists Wentzel, Kramers and Brillouin, who all developed the approach independently in 1926.4 Earlier, in 1923, the mathematician Harold Jeffreys had developed a general method of approximating the general class of linear, second-order


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differential equations, which of course includes the Schrödinger equation.\(^5\) But since the Schrödinger equation was developed two years later, and Wentzel, Kramers, and Brillouin were apparently unaware of this earlier work, the contribution of Jeffreys is often neglected.

The WKB method is important both as a practical means of approximating solutions to the Schrödinger equation, and also as a conceptual framework for understanding the classical limit of quantum mechanics. The WKB approximation is valid whenever the wavelength, \(\lambda\), is small in comparison to other relevant length scales in the problem. This condition is not restricted to quantum mechanics, but rather can be applied to any wave-like system (such as fluids, electromagnetic waves, etc.), where it leads to approximation schemes which are mathematically very similar to the WKB method in quantum mechanics. For example, in optics the approach is called the eikonal method, and in general the method is referred to as short wavelength asymptotics. Whatever the name, the method is an old one, which predates quantum mechanics – indeed, it was apparently first used by Liouville and Green in the first half of the nineteenth century. In quantum mechanics, \(\lambda\) is interpreted as the de Broglie wavelength, and \(L\) is normally the length scale of the potential. Thus, the WKB method is valid if the wavefunction oscillates many times before the potential energy changes significantly.

### 7.4.1 Semi-classical approximation to leading order

Consider then the propagation of a quantum particle in a slowly-varying one-dimensional potential, \(V(x)\). Here, by “slowly-varying” we mean that, in any small region the wavefunction is well-approximated by a plane wave, and that the wavelength only changes over distances that are long compared with the local value of the wavelength. We’re also assuming for the moment that the particle has positive kinetic energy in the region. Under these conditions, we can anticipate that the solution to the time-independent Schrödinger equation

\[
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x) \psi(x) = E \psi(x),
\]

will take the form \(A(x)e^{\pm ip(x)x/\hbar}\) where \(p(x)\) is the “local” value of the momentum set by the classical value, \(p^2/2m + V(x) = E\), and the amplitude, \(A(x)\), is slowly-varying compared with the phase factor. Clearly this is a semi-classical limit: \(\hbar\) has to be sufficiently small that there are many oscillations in the typical distance over which the potential varies.\(^6\)

To develop this idea a little more rigorously, and to emphasize the rapid phase variation in the semi-classical limit, we can parameterize the wavefunction as

\[
\psi(x) = e^{i\sigma(x)/\hbar}.
\]


\(^6\)To avoid any point of confusion, it is of course true that \(\hbar\) is a fundamental constant – not easily adjusted! So what do we mean when we say that the semi-classical limit translates to \(\hbar \to 0^+\)? The validity of the semi-classical approximation relies upon \(\lambda/L \ll 1\). Following the de Broglie relation, we may write this inequality as \(\hbar/pL \ll 1\), where \(p\) denotes the particle momentum. Now, in this correspondence, both \(p\) and \(L\) can be considered as “classical” scales. So, formally, we can think of think of accessing the semi-classical limit by adjusting \(\hbar\) so that it is small enough to fulfil this inequality. Alternatively, at fixed \(\hbar\), we can access the semi-classical regime by reaching to higher and higher energy scales (larger and larger \(p\)) so that the inequality becomes valid.
Here the complex function \( \sigma(x) \) encompasses both the amplitude and phase. Then, with \(-\hbar^2 \partial_x^2 \psi(x) = -i\hbar e^{i\sigma(x)/\hbar} \partial_x^2 \sigma(x) + e^{i\sigma(x)/\hbar} (\partial_x \sigma)^2\), the Schrödinger equation may be rewritten in terms of the phase function as,

\[
-i\hbar \partial_x^2 \sigma(x) + (\partial_x \sigma)^2 = p^2(x).
\]

(7.9)

Now, since we’re assuming the system is semi-classical, it makes sense to expand \( \sigma(x) \) as a power series in \( \hbar \) setting, \( \sigma = \sigma_0 + (\hbar/i) \sigma_1 + (\hbar/i)^2 \sigma_2 + \cdots \).

At the leading (zeroth) order of the expansion, we can drop the first term in (7.9), leading to \((\partial_x \sigma_0)^2 = p^2(x)\). Fixing the sign of \( p(x) \) by \( p(x) = +\sqrt{2m(E - V(x))} \), we conclude that

\[
\sigma_0(x) = \pm \int p(x) dx.
\]

For free particle systems – those for which the kinetic energy is proportional to \( p^2 \) – this expression coincides with the classical action.

From the form of the Schrödinger equation (7.9), it is evident that this approximate solution is only valid if we can ignore the first term. More precisely, we must have

\[
\left| \frac{\hbar \partial_x^2 \sigma(x)}{(\partial_x \sigma(x))^2} \right| \equiv \left| \frac{\partial_x (\hbar/\partial_x \sigma)}{\partial_x \sigma} \right| \ll 1.
\]

But, in the leading approximation, \( \partial_x \sigma \approx p(x) \) and \( p(x) = 2\pi \hbar/\lambda(x) \), so the condition translates to the relation

\[
\frac{1}{2\pi} |\partial_x \lambda(x)| \ll 1.
\]

This means that the change in wavelength over a distance of one wavelength must be small. Obviously, this condition can not always be met: In particular, if the particle is confined by an attractive potential, at the edge of the classically allowed region, where \( E = V(x) \), \( p(x) \) must be zero and the corresponding wavelength infinite. The approximation is only valid well away from these classical turning points, a matter to which we will return shortly.

### 7.4.2 Next to leading order correction

Let us now turn to the next term in the expansion in \( \hbar \). Retaining terms from Eq. (7.9) which are of order \( \hbar \), we have

\[
-i\hbar \partial_x^2 \sigma_0 + 2\partial_x \sigma_0 (\hbar/i) \partial_x \sigma_1 = 0.
\]

Rearranging this equation, and integrating, we find

\[
\partial_x \sigma_1 = -\frac{\partial_x^2 \sigma_0}{2\partial_x \sigma_0} = -\frac{\partial_x p}{2p}, \quad \sigma_1(x) = -\frac{1}{2} \ln p(x).
\]

So, to this order of approximation, the wavefunction takes the form,

\[
\psi(x) = \frac{C_1}{\sqrt{p(x)}} e^{i\hbar \int p dx} + \frac{C_2}{\sqrt{p(x)}} e^{-i\hbar \int p dx},
\]

(7.10)

where \( C_1 \) and \( C_2 \) denote constants of integration. To interpret the factors of \( \sqrt{p(x)} \), consider the first term: a wave moving to the right. Since \( p(x) \) is real
(remember we are currently considering the classically allowed region where \( E > V(x) \)), the exponential has modulus unity, and the local probability density is proportional to \( 1/p(x) \), i.e. to \( 1/v(x) \), where \( v(x) \) denotes the velocity of the particle. This dependence has a simple physical interpretation: the probability of finding the particle in any given small interval is proportional to the time it spends there. Hence it is inversely proportional to its speed.

We turn now to consider the wavefunction in the classically forbidden region where

\[
\frac{p^2(x)}{2m} = E - V(x) < 0.
\]

Here \( p(x) \) is of course pure imaginary, but the same formal phase solution of the Schrödinger equation applies provided, again, that the particle is remote from the classical turning points where \( E = V(x) \). In this region, the wavefunction takes the general form,

\[
\psi(x) = \frac{C_1}{\sqrt{|p(x)|}} e^{-(1/\hbar) \int |p| \, dx} + \frac{C_2}{\sqrt{|p(x)|}} e^{(1/\hbar) \int |p| \, dx}.
\]

This completes our study of the wavefunction in the regions in which the semi-classical approach can be formally justified. However, to make use of this approximation, we have to understand how to deal with the regions close to the classical turning points. Remember in our treatment of the Schrödinger equation, energy quantization derived from the implementation of boundary conditions.

### 7.4.3 Connection formulae, boundary conditions and quantization rules

Let us assume that we are dealing with a one-dimensional confining potential where the classically allowed region is unique and spans the interval \( b \leq x \leq a \). Clearly, in the classically forbidden region to the right, \( x > a \), only the first term in Eq. (7.11) remains convergent and can contribute while, for \( x < b \) it is only the second term that contributes. Moreover, in the classically allowed region, \( b \leq x \leq a \), the wavefunction has the oscillating form (7.10).

But how do we connect the three regions together? To answer this question, it is necessary to make the assumption that the potential varies sufficiently smoothly that it is a good approximation to take it to be linear in the vicinity of the classical turning points. That is to say, we assume that a linear potential is a sufficiently good approximation out to the point where the short wavelength (or decay length for tunneling regions) description is adequate. Therefore, near the classical turning at \( x = a \), we take the potential to be

\[
E - V(x) \approx F_0(x - a),
\]

where \( F_0 \) denotes the (constant) force. For a strictly linear potential, the wavefunction can be determined analytically, and takes the form of an Airy function.\(^7\) In particular, it is known that the Airy function to the right of the classical turning point has the asymptotic form

\[
\lim_{x \to a^+} \psi(x) = \frac{C}{2\sqrt{|p(x)|}} e^{-(1/\hbar) \int_a^x |p| \, dx},
\]

\(^7\)For a detailed discussion in the present context, we refer to the text by Landau and Lifshitz.

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The classical momentum is given by
\[ \text{orbitO} \rightarrow \text{M} \]
\[ \Delta \text{the orbital frequency of the particleO} \]
one photon and drops to the next levelM the frequency of the photon emitted is just
\[ \Delta \text{of phase space S} \]
\[ s = \text{classical path in phase spaceO} \]
\[ \rightarrow \text{his shows that each state is associated with an element} \]
\[ \Delta \text{levels are as expected specified by} \]
\[ \text{the last term reflecting the two turning pointsO} \]
\[ \text{his is just the} \]
\[ \partial E \]
\[ \text{whereM for} \]
\[ \text{he classical turning points are set by} \]
\[ \partial E \]
\[ \text{it has the asymptotic oscillatory solutionM translating to a decay into the classically forbidden region while, to the left,} \]
\[ \text{it has the asymptotic oscillatory solution,} \]
\[ \lim_{b \to \infty} \psi(x) = \frac{C}{\sqrt{p(x)}} \cos \left( \frac{1}{\hbar} \int_x^b p(x) dx - \frac{\pi}{4} \right) = \frac{C}{\sqrt{p(x)}} \cos \left( \frac{\pi}{4} - \frac{1}{\hbar} \int_x^b p(x) dx \right). \]
At the second classical turning point at \( x = b \), the same argument gives
\[ \lim_{b \to \infty} \psi(x) = \frac{C'}{\sqrt{p(x)}} \cos \left( \frac{1}{\hbar} \int_x^b p(x) dx - \frac{\pi}{4} \right). \]
For these two expressions to be consistent, we must have \( C' = \pm C \) and
\[ \left( \frac{1}{\hbar} \int_x^b p(x) dx - \frac{\pi}{4} \right) - \left( \frac{\pi}{4} - \frac{1}{\hbar} \int_x^a p(x) dx \right) = n\pi, \]
where, for \( n \) even, \( C' = C \) and for \( n \) odd, \( C' = -C \). Therefore, we have the condition \( \frac{1}{\hbar} \int_x^b p(x) dx = (n + 1/2)\pi \), or when cast in terms of a complete periodic cycle of the classical motion,
\[ \oint p dx = 2\pi \hbar(n + 1/2). \]
This is just the Bohr-Sommerfeld quantization condition, and \( n \) can be interpreted as the number of nodes of the wavefunction.

**INFO.** Note that the integrated action, \( \oint p dx \), represents the area of the classical path in phase space. This shows that each state is associated with an element of phase space \( 2\pi \hbar \). From this, we can deduce the approximate energy splitting between levels in the semi-classical limit: The change in the integral with energy \( \Delta E \) corresponding to one level must be \( 2\pi \hbar \) — one more state and one more node, i.e. \( \Delta E \partial \psi \oint p dx = 2\pi \hbar \). Now the energy \( E = \psi \), so \( \partial E \partial p dx = \oint dx = T \), the period of the orbit. Therefore, \( \Delta E = 2\pi \hbar/T = \hbar \omega \): In the semi-classical limit, if a particle emits one photon and drops to the next level, the frequency of the photon emitted is just the orbital frequency of the particle.

**EXAMPLE:** For the quantum harmonic oscillator, \( H = \frac{p^2}{2m} + \frac{1}{2} \hbar \omega^2 x^2 = E \), the classical momentum is given by
\[ p(x) = \sqrt{2m \left( E - \frac{\hbar \omega^2 x^2}{2} \right)} . \]
The classical turning points are set by \( E = \hbar \omega^2 x_0^2/2 \), i.e. \( x_0 = \pm 2E/\hbar \omega^2 \). Over a periodic cycle, the classical action is given by
\[ \oint p(x) dx = 2 \int_{-x_0}^{x_0} dx \sqrt{2m \left( E - \frac{\hbar \omega^2 x^2}{2} \right)} = 2\pi \frac{E}{\omega} . \]
According to the WKB method, the latter must be equated to \( 2\pi \hbar(n + 1/2) \), with the last term reflecting the two turning points. As a result, we find that the energy levels are as expected specified by \( E_n = (n + 1/2)\hbar \omega \).

In the WKB approximation, the corresponding wavefunctions are given by
\[ \psi(x) = \frac{C}{\sqrt{p(x)}} \cos \left( \frac{1}{\hbar} \int_{-x_0}^x p(x) dx - \frac{\pi}{4} \right) = \frac{C}{\sqrt{p(x)}} \cos \left( \frac{2\pi}{4}(n + 1/2) + \frac{1}{\hbar} \int_{-x_0}^x p(x) dx - \frac{\pi}{4} \right) = \frac{C}{\sqrt{p(x)}} \cos \left( \frac{n\pi}{2} + \frac{E}{\hbar \omega} \left[ \arcsin \left( \frac{x}{x_0} \right) + \frac{x}{x_0} \sqrt{1 - \frac{x^2}{x_0^2}} \right] \right) . \]

The WKB wavefunction (solid) and the exact wavefunction (dashed) for the \( n = 0 \) and \( n = 10 \) states of the quantum harmonic oscillator.
for \(0 < x < x_0\) and
\[
\psi(x) = \frac{C}{2\sqrt{p(x)}} \exp \left( -\frac{E}{\hbar \omega} \left[ \frac{x}{x_0} \sqrt{\frac{x^2}{x_0^2} - 1 - \text{arccosh} \left( \frac{x}{x_0} \right)} \right] \right).
\]

for \(x > a\). Note that the failure of the WKB approximation is reflected in the appearance of discontinuities in the wavefunction at the classical turning points (see figures). Nevertheless, the wavefunction at high energies provide a strikingly good approximation to the exact wavefunctions.

\begin{itemize}
\item **Example:** As a second example, let us consider the problem of quantum tunneling. Suppose that a beam of particles is incident upon a localized potential barrier, \(V(x)\). Further, let us assume that, over a single continuous region of space, from \(b\) to \(a\), the potential rises above the incident energy of the incoming particles so that, classically, all particles would be reflected. In the quantum system, the some particles incident from the left may tunnel through the barrier and continue propagating to the right. We are interested in finding the transmission probability.

From the WKB solution, to the left of the barrier (region 1), we expect a wavefunction of the form
\[
\psi_1(x) = \frac{1}{\sqrt{p}} \exp \left[ \frac{i}{\hbar} \int_b^x p \, dx \right] + r(E) \frac{1}{\sqrt{p}} \exp \left[ -\frac{i}{\hbar} \int_b^x p \, dx \right],
\]

with \(p(E) = \sqrt{2m(E-V(x))}\), while, to the right of the barrier (region 3), the wavefunction is given by
\[
\psi_3(x) = t(E) \frac{1}{\sqrt{p}} \exp \left[ i \int_a^x p \, dx \right].
\]

In the barrier region, the wavefunction is given by
\[
\psi_2(x) = \frac{C_1}{\sqrt{|p(x)|}} \exp \left[ -\frac{1}{\hbar} \int_a^x |p| \, dx \right] + \frac{C_2}{\sqrt{|p(x)|}} \exp \left[ \frac{1}{\hbar} \int_a^x |p| \, dx \right].
\]

Then, applying the continuity condition on the wavefunction and its derivative at the classical turning points, one obtains the transmissivity,
\[
T(E) \approx \exp \left[ -\frac{2}{\hbar} \int_a^b |p| \, dx \right].
\]

\begin{itemize}
\item **Info:** For a particle strictly confined to one dimension, the connection formulae can be understood within a simple picture: The wavefunction “spills over” into the classically forbidden region, and its twisting there collects an \(\pi/4\) of phase change. So, in the lowest state, the total phase change in the classically allowed region need only be \(\pi/2\). For the radial equation, assuming that the potential is well behaved at the origin, the wavefunction goes to zero there. A bound state will still spill over beyond the classical turning point at \(r_0\), say, but clearly there must be a total phase change of \(3\pi/4\) in the allowed region for the lowest state, since there can be no spill over to negative \(r\). In this case, the general quantization formula will be
\[
\frac{1}{\hbar} \int_0^{r_0} p(r) \, dr = (n + 3/4)\pi, \quad n = 0, 1, 2, \ldots,
\]

with the series terminating if and when the turning point reaches infinity. In fact, some potentials, including the Coulomb potential and the centrifugal barrier for \(\ell \neq 0\), are in fact singular at \(r = 0\). These cases require special treatment.
\end{itemize}