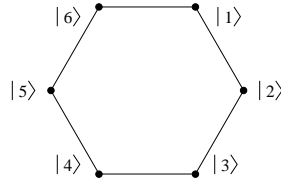


Homework Set #4 – Solutions

1. A molecule is composed of six identical atoms which form a regular hexagon. Consider a single electron which can be localized on any one of the atoms. Let $|n\rangle$ denote the state in which it is localized on the n -th atom. (This is a six-dimensional Hilbert space, spanned by the states $|1\rangle$ through $|6\rangle$.)



Let R be the discrete rotation operator, $R|i\rangle = |i + 1\rangle$ (where we let $|7\rangle \equiv |1\rangle$ and $|0\rangle \equiv |6\rangle$). We assume that the Hamiltonian has the form

$$H = \sum_{i=1}^6 \left(E_0 |i\rangle\langle i| - \lambda (|i\rangle\langle i + 1| + |i\rangle\langle i - 1|) \right)$$

(λ represents a nearest-neighbor electron hopping interaction).

- a) Find the eigenvalues and eigenstates of R , and show that they are non-degenerate.

Since R is the discrete clockwise rotation operator, it is easy to see that if we act with R six times, we end up with the identity, $R^6|\psi\rangle = |\psi\rangle$. This indicates that the eigenvalues of R may be the sixth roots of unity

$$R|\psi_k\rangle = \omega^k|\psi\rangle, \quad \omega = e^{\pi i/3} \tag{1}$$

Strictly speaking, we do not yet know that all the distinct sixth roots of unity show up non-degenerately as eigenvalues. However, we can go ahead and construct the eigenstates and show that they do correspond to non-degenerate roots. To do so, we write

$$|\psi_k\rangle = \sum_{i=1}^6 c_i |i\rangle$$

and substitute it into the eigenvalue equation (1). This results in a set of equations $c_{i+1} = \omega^{-k}c_i$ (with periodicity implied on i). The solution is then $c_i = \omega^{-ki}$ (where i is an index). With standard normalization, we find

$$|\psi_k\rangle = \frac{1}{\sqrt{6}} \sum_{i=1}^6 \omega^{-ki} |i\rangle, \quad \text{eigenvalue} = \omega^k \tag{2}$$

Since we have constructed six states all with distinct eigenvalues, they are obviously non-degenerate. Note that these states are a discrete version of Bloch wavefunctions. After all, this ring is essentially a one-dimensional lattice with periodic boundary conditions.

Since the structure is a regular hexagon, the rotation operator R forms part of the symmetry group of the molecule. The complete symmetry group of the hexagon is the dihedral group D_6 , which may be generated by the rotation R along with a “reflection”.

- b) Show that R commutes with the Hamiltonian, and find the eigenvalues and eigenstates of H .

Note that the rotation operator R may be written as

$$R = \sum_{i=1}^6 |i\rangle\langle i-1|$$

while its inverse is

$$R^{-1} = R^5 = \sum_{i=1}^6 |i\rangle\langle i+1|$$

Hence the Hamiltonian may be written as

$$H = E_0 I - \lambda(R^{-1} + R) \quad (3)$$

where I is the identity operator. Since R commutes with itself and its inverse (and clearly with the identity as well), we see that R commutes with H . Since $[R, H] = 0$, we may find simultaneous eigenstates of both R and H . In particular, the non-degenerate states found in a) above must also be eigenstates of H . It should be obvious from (1) and (3) that the eigenenergies of H are given by

$$E_k = E_0 - \lambda(\omega^{-k} + \omega^k) = E_0 - 2\lambda \cos(k\pi/3)$$

where the k th eigenstate is given in (2). This problem is easily generalized to a regular n -gon, corresponding to a lattice with n sites and with periodic boundary conditions. In this case, k is essentially a Bloch momentum, and the eigenenergy is simply that of a Bloch wave (ie it has a standard dispersion relation for small k , but eventually turns around because of the periodicity).

2. Show that, to next order in the semi-classical expansion, the WKB wavefunction may be written as

$$\psi(x) = \frac{1}{\sqrt{k(x)}} e^{\pm i \int k(x) dx} \left[1 \mp \frac{i\hbar}{4} \left(m \frac{F(x)}{p^3(x)} + \frac{1}{2} m^2 \int \frac{F^2(x)}{p^5(x)} dx \right) + \dots \right]$$

where $p(x) = \hbar k(x)$, and $F(x) = p'(x)p(x)/m$ is the classical force. Explain why the second order term may often be neglected, while the first order term (the $1/\sqrt{k(x)}$ factor) should be retained in the WKB approximation.

Write the WKB wavefunction as

$$\psi(x) = e^{iu(x)} = \exp\left(\frac{i}{\hbar}(u_0(x) + \hbar u_1(x) + \hbar^2 u_2(x) + \dots)\right)$$

where $u(x)$ satisfies $u'^2(x) - \hbar^{-2}p^2(x) = iu''(x)$. Expanding $u(x)$, we obtain, for the first few orders

$$u_0'^2(x) = p^2(x), \quad 2u_0'(x)u_1'(x) = iu_0''(x), \quad 2u_0'(x)u_2'(x) + u_1'^2(x) = iu_1''(x)$$

The lowest order equation is solved by

$$u_0'(x) = \pm p(x) \quad \longrightarrow \quad u_0(x) = \pm \int p(x) dx \quad (4)$$

The next order equation then gives

$$u_1'(x) = \frac{i}{2}(\log |u_0'(x)|)' = \frac{i}{2}(\log p(x))' \quad \longrightarrow \quad u_1(x) = \frac{i}{2} \log p(x) \quad (5)$$

So far, this gives the “standard” WKB approximation. Now we examine the next higher order term

$$u_2'(x) = -\frac{1}{2} \frac{u_1'^2(x)}{u_0'(x)} + \frac{i}{2} \frac{u_1''(x)}{u_0'(x)}$$

Substituting in (4) and (5) yields

$$\pm u_2'(x) = -\frac{1}{4} \frac{p''(x)}{p^2(x)} + \frac{3}{8} \frac{p'^2(x)}{p^3(x)} = -\frac{1}{4} \left(\frac{p'(x)}{p^2(x)} \right)' - \frac{1}{8} \frac{p'^2(x)}{p^3(x)}$$

Hence

$$u_2(x) = \mp \frac{1}{4} \left(\frac{p'(x)}{p^2(x)} + \frac{1}{2} \int \frac{p'^2(x)}{p^3(x)} dx \right)$$

Substituting in $p'(x) = mF(x)/p(x)$, we obtain

$$u_2(x) = \mp \frac{1}{4} \left(m \frac{F(x)}{p^3(x)} + \frac{1}{2} m^2 \int \frac{F^2(x)}{p^5(x)} dx \right) \quad (6)$$

Finally, this allows us to write

$$\begin{aligned} \psi(x) &= e^{\frac{i}{\hbar}u_0(x) + iu_1(x) + i\hbar u_2(x) + \dots} \\ &= \frac{1}{\sqrt{p(x)}} e^{\pm \frac{i}{\hbar} \int p(x) dx} (1 + i\hbar u_2(x) + \dots) \end{aligned}$$

where we have expanded the exponential $e^{i\hbar u_2(x)}$ for small \hbar . Then substituting in (6) for $u_2(x)$ gives the correct result.

The reason that the $u_2(x)$ term may generally be neglected is that this term is the first time where \hbar shows up as a small quantity. This is the same reason why we may expand the exponential and keep only the $\mathcal{O}(\hbar)$ term. Note that there is a hidden $\sqrt{\hbar}$ in the prefactor when converting between $p(x)$ and $k(x)$. However this is simply an overall factor, and is unimportant (since we have not normalized the wavefunctions).

3. A neutron falling in a gravitational field and bouncing off a horizontal mirror exhibits quantized energy levels [see Nesvizhevsky *et al.*, Nature **415** (2002) 297]. The potential felt by the neutron is essentially

$$V(z) = \begin{cases} mgz & z > 0 \\ \infty & z < 0 \end{cases}$$

- a) Use the WKB bound state condition for turning points at $z = 0$ and $z = E/mg$ to find the quantized energy levels of the bouncing neutron. Write down the first three energy levels in units of $(mg^2\hbar^2)^{1/3}$.

The WKB bound state condition is $\varphi = (n + \frac{1}{2})\pi$ where

$$\varphi = \int_b^a k(z) dz \quad (7)$$

For this potential, $\hbar k = \sqrt{2m(E - mgz)}$, and the turning points are $z = 0$ and $z = E/mg$. Thus

$$\varphi = \hbar^{-1} \int_0^{E/mg} \sqrt{2m(E - mgz)} dz = \sqrt{\frac{2mE}{\hbar^2}} \int_0^{E/mg} \sqrt{1 - mgz/E} dz$$

We perform a change of variables, $u = mgz/E$ to obtain

$$\varphi = \sqrt{\frac{2E^3}{mg^2\hbar^2}} \int_0^1 \sqrt{1-u} du = -\sqrt{\frac{2E^3}{mg^2\hbar^2}} \frac{2}{3} (1-u)^{3/2} \Big|_0^1 = \sqrt{\frac{8E^3}{9mg^2\hbar^2}}$$

Setting this equal to $(n + \frac{1}{2})\pi$ and solving for E , we find

$$E^3 = (mg^2\hbar^2) \frac{9\pi^2}{8} (n + \frac{1}{2})^2$$

In units of $(mg^2\hbar^2)$, the first three energy levels are

$$E_0 = 1.4054, \quad E_1 = 2.9233, \quad E_2 = 4.1094$$

- b) Note that this potential is essentially half of the absolute value potential $V(z) = mg|z|$ [see Merzbacher pp. 123–125]. However, for the neutron, because of the mirror at $z = 0$, we must impose a boundary condition $\psi(0) = 0$. This is equivalent to finding odd-parity solutions of the $V(z) = mg|z|$ problem.

Find a WKB expression for the odd-parity energy levels of the $V(z) = mg|z|$ problem. Again, write down the first three energy levels in units of $(mg^2\hbar^2)^{1/3}$.

For the absolute value potential, the turning points are at $z = -E/mg$ and $z = E/mg$. Thus the WKB condition is essentially the same as computed above,

except that the integral is from negative to positive limits. Thus φ is twice the value as in a), resulting in the condition

$$E^3 = (mg^2\hbar^2) \frac{9\pi^2}{32} (n + \frac{1}{2})^2$$

This is just the result given in the textbook (except that we have defined the potential with a factor of mass m). For the odd-parity levels, we want n to be odd. Letting $n \rightarrow 2n + 1$, this results in the new bouncing ball WKB approximation

$$E^3 = (mg^2\hbar^2) \frac{9\pi^2}{8} (n + \frac{3}{4})^2$$

The first three energy levels computed in this fashion are

$$E_0 = 1.8416, \quad E_1 = 3.2397, \quad E_2 = 4.3790$$

- c) Compare your energies from parts a) and b) with the exact values (in units of $(mg^2\hbar^2)^{1/3}$)

$$E_0 = 1.8558, \quad E_1 = 3.2446, \quad E_2 = 4.3817$$

(for the neutron, $E_0 \approx 1.41 \times 10^{-12}$ eV). Which approximation is the better one, and why?

Comparison of the above energies indicates that the WKB approximation of part b) is the better one (less than 1% error in the ground state energy, and less than a tenth of a percent in the second excited state). The only difference in the two approximations is the $\frac{1}{2}$ versus $\frac{3}{4}$ in the expressions. In the semi-classical picture, these factors account for a bit of tunneling of the wavefunction into the classically forbidden regions. In fact, we recall that the WKB bound state condition assumes that there is a bit of tunneling at the turning points. However, in part a), the infinite barrier at $z = 0$ prevents any tunneling. Thus simple application of WKB in part a) is not really valid, whereas the odd-parity approach of part b) does enforce the proper vanishing of the wavefunction at $z = 0$.

Of course, we could have directly derived a modified WKB bound state condition based on the vanishing of the WKB wavefunction at $z = 0$. The result would then be $\varphi = (n + \frac{3}{4})\pi$ where φ is the integral of (7). Similarly, we would find $\varphi = (n+1)\pi$ if the WKB wavefunction had to vanish at both turning points. This latter simply corresponds to the Bohr-Sommerfeld quantization condition.

4. For a spherically symmetric potential, the radial equation for $u(r)$, where $\psi(r, \theta, \varphi) = r^{-1}u(r)Y_\ell^m(\theta, \varphi)$, is effectively one-dimensional

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + V_{\text{eff}}(r)u = Eu, \quad V_{\text{eff}}(r) = V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}$$

As a result, we may apply WKB to $u(r)$, however with a slight refinement of using

$$V_{\text{WKB}}(r) = V(r) + \frac{\hbar^2(\ell + \frac{1}{2})^2}{2mr^2}$$

instead of V_{eff} . Show that the WKB bound state condition gives the exact energy levels for both the hydrogen atom ($V(r) = -e^2/r$) and the three-dimensional harmonic oscillator ($V(r) = \frac{1}{2}m\omega^2r^2$). You may want to use the integral

$$\int_a^b \frac{dr}{r} \sqrt{-(r-a)(r-b)} = \frac{\pi}{2}(a+b-2\sqrt{ab}), \quad 0 < a < b$$

In general, the bound state condition is given by $\varphi = (n + \frac{1}{2})\pi$ where

$$\begin{aligned} \varphi &= \hbar^{-1} \int_a^b \sqrt{2m(E - V_{\text{WKB}}(r))} dr \\ &= \hbar^{-1} \int_a^b \sqrt{2m(E - V(r) - \hbar^2(\ell + \frac{1}{2})^2/2mr^2)} dr \end{aligned}$$

The turning points, a and b , correspond to the values of r where the argument of the square root vanish.

For the hydrogen atom, we have

$$\begin{aligned} \varphi &= \hbar^{-1} \int_a^b \sqrt{2m(E + e^2/r - \hbar^2(\ell + \frac{1}{2})^2/2mr^2)} dr \\ &= \sqrt{2m|E|} \hbar^{-1} \int_a^b \sqrt{-r^2 + e^2r/|E| - \hbar^2(\ell + \frac{1}{2})^2/2m|E|} \frac{dr}{r} \end{aligned}$$

where we note that the energy E is negative. This integral is in the form given above, where the sum and product of the roots are

$$a + b = \frac{e^2}{|E|}, \quad ab = \frac{\hbar^2(\ell + \frac{1}{2})^2}{2m|E|}$$

As a result, we find

$$\varphi = \sqrt{2m|E|} \frac{\pi}{2\hbar} \left(\frac{e^2}{|E|} - 2\hbar \frac{\ell + \frac{1}{2}}{\sqrt{2m|E|}} \right) = \frac{\pi\sqrt{me^2}}{\sqrt{2|E|}\hbar} - (\ell + \frac{1}{2})\pi$$

Setting this equal to $(n + \frac{1}{2})\pi$, we finally obtain

$$E = -\frac{me^4}{2\hbar^2(n + \ell + 1)^2}$$

(where we recall that E is negative). This is the exact expression for the hydrogen eigenenergies, provided we identify the principle quantum number with $n + \ell + 1$. In fact, this is the correct identification, as here n gives the number of nodes in the WKB wavefunction (ie radial wavefunction), while the principle quantum number counts both radial and spherical harmonic nodes (and starts from one instead of zero).

For the three-dimensional harmonic oscillator, the WKB integral is instead

$$\begin{aligned}\varphi &= \hbar^{-1} \int_a^b \sqrt{2m \left(E - \frac{1}{2}m\omega^2 r^2 - \hbar^2(\ell + \frac{1}{2})^2/2mr^2 \right)} dr \\ &= \frac{m\omega}{\hbar} \int_a^b \sqrt{-r^4 + 2Er^2/m\omega^2 - \hbar^2(\ell + \frac{1}{2})^2/m^2\omega^2} \frac{dr}{r}\end{aligned}$$

This is not quite in the form we want for the integration formula. However, we may make a change of variables, $x = r^2$, to obtain

$$\varphi = \frac{m\omega}{2\hbar} \int_a^b \sqrt{-x^2 + 2Ex/m\omega^2 - \hbar^2(\ell + \frac{1}{2})^2/m^2\omega^2} \frac{dx}{x}$$

Since the sum and products of the roots are

$$a + b = \frac{2E}{m\omega^2}, \quad ab = \frac{\hbar^2(\ell + \frac{1}{2})^2}{m^2\omega^2}$$

we find

$$\varphi = \frac{m\omega}{2\hbar} \frac{\pi}{2} \left(\frac{2E}{m\omega^2} - 2\hbar \frac{\ell + \frac{1}{2}}{m\omega} \right) = \frac{\pi}{2} \left(\frac{E}{\hbar\omega} - (\ell + \frac{1}{2}) \right)$$

Since $\varphi = (n + \frac{1}{2})\pi$, we find

$$E = (2n + \ell + \frac{3}{2})\hbar\omega$$

which turns out to be the correct expression for the three-dimensional harmonic oscillator. Note again that the WKB n counts the number of nodes in the radial wavefunction. The zero-point energy $\frac{3}{2}\hbar\omega$ is simple to understand. To see why the other part is $2n + \ell$ and not something like $n + \ell$ requires an understanding of the oscillator in terms of a spherical harmonic (angular momentum) basis. A quick way to see why the energy changes by $2\hbar\omega$ when n is increased by a single unit is to recall that the harmonic oscillator states alternate between even and odd parity. However states of a given angular momentum ℓ must all have the same parity (even and odd parity for even and odd ℓ , respectively). As a result, energies for a given angular momentum can only jump by an even number of units.

It is somewhat remarkable that these WKB calculations give the exact eigenenergies of these three-dimensional systems. Actually, these two potentials ($1/r$ and r^2) are rather ‘special’, as they are the only two central potentials that lead to closed classical orbits. In this sense, they have additional symmetries, and this gives a hint, at least, as to why the WKB result is exact.