General Exam Part II, Fall 1998
Quantum Mechanics Solutions

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Problem 1

Consider a particle of charge q and mass m confined to the x-y plane and subject to a harmonic oscillator potential $V = \frac{1}{2}m\omega^2\left(x^2+y^2\right)$ and a uniform electric field of magnitude E oriented along the positive x-direction.

(a) What is the Hamiltonian for the system?

Solution: The electric potential Φ satisfies $E = -\nabla\Phi$. Up to an ignorable constant, we have $\Phi = -Ex$ and the potential for a charge q in this field is $V_e = -qEx$. The full Hamiltonian is

$$H = \frac{p_x^2+p_y^2}{2m} + \frac{1}{2}m\omega^2\left(x^2+y^2\right) - qEx.$$

(b) What are the eigenvalues and associated degeneracies for this Hamiltonian?

Solution: Note that one may rewrite the Hamiltonian as

$$H = \frac{p_x^2+p_y^2}{2m} + \frac{1}{2}m\omega^2\left((x-d)^2+y^2\right) - \frac{1}{2}m\omega^2 d^2,$$

where d is a characteristic distance, $d = \frac{qE}{m\omega^2}$. The application of the electric field has translated the center of the harmonic oscillator and shifted the spectrum by a constant energy. From the well known harmonic oscillator problem, we have

$$H = \hbar\omega\left(N_{x,E} + N_y + 1\right) - \frac{q^2E^2}{2m\omega^2},$$

with $N_x, N_y \in \{0,1,2,\ldots\}$. The degeneracy of the energy eigenvalue $\hbar\omega(n+1) - q^2E^2/2m\omega^2$, $n \geq 0$, is the number of ways to add an ordered pair of non-negative integers to get n, which is $n+1$.

Now assume the particle is in the ground state of this system.

(c) If the electric field is suddenly turned off, show that the probability of finding the particle with energy $(n+1)\hbar\omega$ is given by a Poisson distribution

$$P(n) = \frac{e^{-\lambda}\lambda^n}{n!}$$

Find λ.

[You may find the following expressions useful:

$$a_x^\dagger = \left(\frac{1}{2m\omega\hbar}\right)^{1/2}(m\omega x - ip_x)$$

and $\exp(A+B) = \exp(A)\exp(B)\exp\left(-\frac{1}{2}[A,B]\right)$ where $[A,B]$ is a c-number.]

Solution: Denote by $|n_x, n_y\rangle_E$ the eigenstates of the system with electric field E. Note first that the x and y oscillators can be treated independently, and second that the electric field affects only the x oscillator. From the first point, it is seen that the state $|n_x, n_y\rangle_E$ may be written purely as a product state $|n_x\rangle_{x,E}|n_y\rangle_{y,E}$. From the second point, it is seen that $|n\rangle_{y,E} = |n\rangle_{y,0} = |n\rangle_y$.

The initial state of the system with some applied field is $|0,0\rangle_E = |0\rangle_{x,E}|0\rangle_y$. When the electric field is turned off, the y oscillator will be unaffected, so the final state must have $n_y = 0$. The only accessible final state with energy $(n+1)\hbar\omega$ and $n_y = 0$ is the state $|n,0\rangle_0 = |n\rangle_{x,0}|0\rangle_y$. The posed problem is now reduced to finding the overlap $\langle n,0|_0|0,0\rangle_E = \langle n|_{x,0}|0\rangle_{x,E}$. The x subscript is dropped from here forward.

First, one constructs $|0\rangle_E$ from the states $|n\rangle_0$. As noted earlier, the electric field simply translates the oscillator, so we may construct this state by a translation on the $E = 0$ states. The momentum operator is the generator of translations, so our state is

$$|0\rangle_E = \exp\left(-idp/\hbar\right)|0\rangle_0$$

where $d = \frac{qE}{m\omega^2}$. The momentum operator can be written in terms of the ladder operators as

$$ip = \left(\frac{m\omega\hbar}{2}\right)^{1/2}\left(a - a^\dagger\right).$$

Now, applying the terminated Baker-Campbell-Hausdorff formula,

$$\begin{aligned} |0\rangle_E &= \exp(\gamma a^\dagger)\exp(-\gamma a)\exp\left(\frac{\gamma^2}{2}[a^\dagger, a]\right)|0\rangle_0 \\ &= \exp(\gamma a^\dagger)\exp(-\gamma a)\exp\left(-\frac{\gamma^2}{2}\right)|0\rangle_0, \end{aligned}$$

from $[a, a^\dagger] = 1$ and where the constants have been lumped into $\gamma = d\left(\frac{m\omega}{2\hbar}\right)^{1/2}$.

The problem has been reduced to calculating the overlap coefficient $c_n = \langle n|_0 \exp(\gamma a^\dagger)\exp(-\gamma a)\exp(-\gamma^2/2)|0\rangle_0$. The 0 subscript is dropped from here

forward, as only $E = 0$ states now appear in the calculations. One may expand the operator exponentials in power series:

$$c_n = \exp(-\gamma^2/2)\langle n| \left(\sum_{j=0}^{\infty} \frac{\gamma^j a^{\dagger j}}{j!} \right) \left(\sum_{k=0}^{\infty} \frac{(-\gamma)^k a^k}{k!} \right) |0\rangle.$$

All terms except for $k = 0$ annihilate $|0\rangle$, so the infinite sum on the right collapses to one term.

$$\begin{aligned} c_n &= \exp(-\gamma^2/2) \sum_{j=0}^{\infty} \frac{\gamma^j}{j!} \langle n|a^{\dagger j}|0\rangle \\ &= \exp(-\gamma^2/2) \sum_{j=0}^{\infty} \frac{\gamma^j}{j!} \langle n|\sqrt{j!}|j\rangle = \exp(-\gamma^2/2) \sum_{j=0}^{\infty} \frac{\gamma^j}{j!} \sqrt{j!}\delta_{nj} \\ &= \exp(-\gamma^2/2) \frac{\gamma^n}{\sqrt{n!}}. \end{aligned}$$

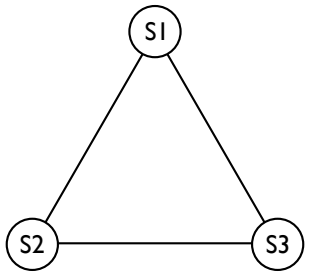
The probability $P(n)$ is the magnitude squared of the overlap c_n,

$$P(n) = \frac{e^{-\gamma^2}\gamma^{2n}}{n!}.$$

One identifies the Poisson parameter λ as $\gamma^2 = d^2 \frac{m\omega}{2\hbar} = \frac{q^2 E^2}{2\hbar m \omega^3}$.

Problem 2

A molecule consisting of three fixed identical atoms in an equilateral triangle captures an extra electron. Assume that in this system the electron is described by a Hamiltonian H. Ignore the spin of the electron and any other electrons already present in the atoms. To obtain the eigenstate of this captured electron we use a simple basis set consisting of one spherically symmetric localized orbital $|S_i\rangle$ on each atom i and assume that they are orthonormal (i.e., $\langle S_i|S_j\rangle = \delta_{ij}$).



(a) Suppose that $\langle S_1|H|S_2\rangle = \langle S_2|H|S_3\rangle = \langle S_3|H|S_1\rangle \equiv V$ are the *only* non-zero matrix elements in this basis set, find the energies for the captured electron. [Hint: Use the fact that one of the eigenvalues is $2V$, which is non-degenerate.]

Solution: One may solve for the roots of the characteristic polynomial by representing the Hamiltonian as a matrix:

$$H = \begin{array}{c} \\ \langle S_1| \\ \langle S_2| \\ \langle S_3| \end{array} \begin{array}{ccc} |S_1\rangle & |S_2\rangle & |S_3\rangle \\ 0 & V & V \\ V & 0 & V \\ V & V & 0 \end{array}$$

$$0 = \det(H - \lambda I) = -\lambda^3 + 2V^3 + 3V^2\lambda.$$

Already knowing that $2V$ is one non-degenerate eigenvalue, the characteristic polynomial may be factored and one needs only solve a quadratic, rather than a cubic, equation. The factorisation of the characteristic polynomial reveals a double root with $E = -V$.

(b) Since H is invariant under rotations by $\frac{2\pi}{3}$, construct all simultaneous eigenstates of energy and rotation for the captured electron. What are the rotational eigenvalues for each eigenstate? [Hint: The rotation operator $R\left(\frac{2\pi}{3}\right)$ satisfies $R^3 = 1$.]

Solution: Since one knows that R and H share eigenvectors, one may construct the eigenvectors from R, which is simpler. The eigenvalues of R are easily found:

$$R^3|\psi\rangle = \lambda^3|\psi\rangle = |\psi\rangle.$$

That is, the eigenvalues λ are the third roots of unity. One of the three eigenvectors is invariant under rotations, while the other two simply accrue a phase shift of $e^{\pm 2\pi i/3}$. One may perform an explicit calculation by using the matrix representation of R ($R|S_1\rangle = |S_2\rangle$, $R|S_2\rangle = |S_3\rangle$, $R|S_3\rangle = |S_1\rangle$),

$$R = \begin{array}{c} \\ \langle S_1| \\ \langle S_2| \\ \langle S_3| \end{array} \begin{array}{ccc} |S_1\rangle & |S_2\rangle & |S_3\rangle \\ 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{array},$$

but it is faster to construct the eigenstates intuitively. The properly normalized state which is invariant under rotations must be completely symmetric,

$$\begin{aligned} |s\rangle &= \left(|S_1\rangle + |S_2\rangle + |S_3\rangle\right)/\sqrt{3} \\ R|s\rangle &= |s\rangle \\ H|s\rangle &= 2V|s\rangle. \end{aligned}$$

The other two eigenvectors must have the same magnitudes for the various particles, but phase differences of $e^{\pm 2\pi i/3}$. These states are

$$\begin{aligned}
|r\rangle &= \left(|S_1\rangle + e^{-2\pi i/3}|S_2\rangle + e^{+2\pi i/3}|S_3\rangle\right)/\sqrt{3} \\
R|r\rangle &= e^{+2\pi i/3}|r\rangle \\
H|r\rangle &= -V|r\rangle \\
|l\rangle &= \left(|S_1\rangle + e^{+2\pi i/3}|S_2\rangle + e^{-2\pi i/3}|S_3\rangle\right)/\sqrt{3} \\
R|l\rangle &= e^{-2\pi i/3}|l\rangle \\
H|l\rangle &= -V|l\rangle.
\end{aligned}$$

These three states form an orthonormal basis for the space.

(c) Suppose that at time $t = 0$ the electron is captured completely by atom #1 in the state $|S_1\rangle$. What is the probability of finding this electron on atom #1 at a later time t? Describe the motion of this electron.

Solution: One decomposes the state $|S_1\rangle$ into the energy eigenstates and uses the linearity of the Schrödinger equation to evolve each component seperately. First, the decomposition: since the states $\{|s\rangle, |r\rangle, |l\rangle\}$ form an orthonormal basis, the state can be decomposed as

$$\begin{aligned}
|\psi\rangle &= \sum_n |n\rangle\langle n|\psi\rangle \\
|S_1\rangle &= |s\rangle\langle s|S_1\rangle + |r\rangle\langle r|S_1\rangle + |l\rangle\langle l|S_1\rangle \\
&= (|s\rangle + |r\rangle + |l\rangle)/\sqrt{3}.
\end{aligned}$$

The time evolution of an energy eigenstate is simple:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle &= \frac{-i}{\hbar}H|\psi\rangle \\
|\psi(t)\rangle &= \exp\left(-i/\hbar \int_0^t H(t')\mathrm{d}t'\right)|\psi(t=0)\rangle \\
|n(t)\rangle &= \exp\left(-itE_n/\hbar\right)|n(t=0)\rangle,
\end{aligned}$$

for a time-independent Hamiltonian with eigenstate $|n\rangle$ with energy E_n. The time evolution of our state of interest is therefore

$$|\psi(t)\rangle = \left(e^{-it2V/\hbar}|s\rangle + e^{itV/\hbar}|r\rangle + e^{itV/\hbar}|l\rangle\right)/\sqrt{3}.$$

To determine the probability of finding the electron on atom #1 at time t, one first needs to evaluate the overlap $\langle S_1|\psi(t)\rangle$,

$$\langle S_1|\psi(t)\rangle = \left(e^{-it2V/\hbar} + 2e^{itV/\hbar}\right)/3 = e^{-it2V/\hbar}\left(1 + 2e^{3itV/\hbar}\right)/3.$$

The probability is the magnitude squared of this quantity,

$$P_1(t) = \left(1 + 4\cos\left(3tV/\hbar\right) + 4\right)/9 = \left(5 + 4\cos\left(3tV/\hbar\right)\right)/9,$$

which starts at 1 at $t = 0$ and can be as small as $1/9$ but never vanishes. The probabilities of being on atoms #2 or #3 are equal and $P_1 + P_{23} = 1$. The motion of the electron may be described as oscillating between being on atom #1 and being delocalized in a state where $p_1 = 1/9, p_2 = p_3 = 4/9$. The frequency of this oscillation is $3V/\hbar$.