I. VARIATIONAL

A. LHO with $1/(1+x^2)$ test function

Find an approximate ground state energy of the linear harmonic oscillator using a testing function $\psi = \frac{A}{1+Bx^2}$, where A is a normalisation constant and B is a parameter. What is the local energy?

Solution:

We first find the value of the normalisation constant A. For the wavefunction to be normalised $\int \psi^* \psi = 1$, therefore

$$
\begin{aligned}
\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx &= \int_{-\infty}^{\infty} \frac{A^2}{(1 + Bx^2)^2} \\
&= A^2 \left(\frac{x}{2(1 + Bx^2)} + \frac{arctan(\sqrt{B}x)}{2\sqrt{B}} \right) |_{-\infty}^{\infty} \\
&= A^2 \frac{arctan(\sqrt{B}x)}{2\sqrt{B}}|_{-\infty}^{\infty} \\
&= \frac{A^2}{2\sqrt{B}}(\pi/2 + \pi/2) \\
&= \frac{A^2 \pi}{2\sqrt{B}} \, .
\end{aligned}
$$

As the result needs to be equal to one, we obtain

$$
A = \sqrt{\frac{2\sqrt{B}}{\pi}} \, .
$$

The Hamiltonian of the LHO reads

$$
H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \, ,
$$

where the first part is the kinetic energy and the latter is the potential energy.

We first evaluate the expectation value of the kinetic energy for the testing function

$$
\begin{aligned}
\langle \psi|T|\psi \rangle &= \frac{2\sqrt{B}}{\pi} \int_{-\infty}^{\infty} \frac{1}{1 + Bx^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \right) \frac{1}{1 + Bx^2} dx \\
&= -\frac{2\sqrt{B}}{\pi} \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{1}{1 + Bx^2} \frac{d}{dx} \frac{-2Bx}{(1 + Bx^2)^2} dx \\
&= -\frac{2\sqrt{B}}{\pi} \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{1}{1 + Bx^2} \left[\frac{2(2Bx)^2}{(1 + Bx^2)^3} - \frac{2B}{(1 + Bx^2)^2} \right] dx \\
&= -\frac{2\sqrt{B}}{\pi} \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left[\frac{8B^2 x^2}{(1 + Bx^2)^4} - \frac{2B}{(1 + Bx^2)^3} \right] dx \, .
\end{aligned}
$$

Omitting the constants, the two terms integrate to $\pi/(16B^{3/2})$ and $3\pi/(8B^{1/2})$, respectively. The final dependence of the kinetic energy on the parameter B is then

$$\langle\psi|T|\psi\rangle = -\frac{2\sqrt{B}}{\pi}\frac{\hbar^2}{2m}\left[8B^2\frac{\pi}{16B^{3/2}} - 2B\frac{3\pi}{8\sqrt{B}}\right]$$
$$= -\frac{2\sqrt{B}}{\pi}\frac{\hbar^2}{2m}\pi\sqrt{B}[\frac{1}{2} - \frac{3}{4}]$$
$$= \frac{\hbar^2 B}{4m} .$$

For the potential energy, we obtain

$$\langle\psi|V|\psi\rangle = \frac{2\sqrt{B}}{\pi}\int_{-\infty}^{\infty}\frac{1}{1+Bx^2}\frac{1}{2}m\omega^2 x^2\frac{1}{1+Bx^2}dx$$
$$= \frac{\sqrt{B}m\omega^2}{\pi}\int_{-\infty}^{\infty}\frac{x^2}{(1+Bx^2)^2}dx .$$

The integral is $\pi/(2B^{3/2})$ so that the kinetic energy dependence is

$$\langle\psi|V|\psi\rangle = \frac{\sqrt{B}m\omega^2}{\pi}\pi/2B^{3/2} = \frac{m\omega^2}{2B} .$$

The total energy then depends on the parameter B as

$$E(B) = \frac{\hbar^2 B}{4m} + \frac{m\omega^2}{2B} .$$

To find the extrema, we differentiate with respect to B

$$\frac{dE(B)}{dB} = \frac{\hbar^2}{4m} - \frac{m\omega^2}{2B^2} .$$

Setting the result to zero gives us the following condition for B:

$$B = \frac{m\omega\sqrt{2}}{\hbar} .$$

The total energy at this value of B is then

$$E = \frac{\hbar^2 B}{4m} + \frac{m\omega^2}{2B}$$
$$= \frac{\omega\hbar\sqrt{2}}{4} + \frac{\omega\hbar}{2\sqrt{2}}$$
$$= \frac{\omega\hbar}{\sqrt{2}} ,$$

which is the final result. Note that the estimate is quite above the exact value of $\frac{\omega\hbar}{2}$. Another thing to note is that the expectation values of the potential and kinetic energies are identical, which is in accordance with the virial theorem.

B. Hydrogen atom with gaussian

Find an estimate of the ground state energy of the hydrogen atom using a test function $\psi = N\exp(-\alpha r^2)$. The Hamiltonian of a hydrogen atom is $H = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0|r|}$.

Useful integrals:

$$\int_0^\infty x^2 e^{-Ax^2} = \frac{1}{4A}\sqrt{\frac{\pi}{A}}$$

$$\int_0^\infty x^4 e^{-Ax^2} = \frac{3}{2A}\frac{1}{4A}\sqrt{\frac{\pi}{A}}$$

Solution:

We first find the normalisation constant N:

$$1 = \langle\psi|\psi\rangle = N^2 \int d^3r\, e^{-2\alpha r^2}$$

The function has a spherical symmetry and thus we change the coordinates to spherical:

$$= N^2 \int_0^\infty r^2 dr \int_0^{2\pi} d\phi \int_0^\pi d\theta sin(\theta) e^{-2\alpha r^2} .$$

Integrating over ϕ and θ yields the usual 4π factor, leading to

$$= N^2 4\pi \int_0^\infty dr r^2 e^{-2\alpha r^2} = N^2 4\pi \sqrt{\frac{\pi}{2\alpha}}\frac{1}{8\alpha} = N^2 \left(\frac{\pi}{2\alpha}\right)^{3/2} .$$

Hence $N = \left(\frac{2\alpha}{\pi}\right)^{3/4}$.

We now calculate the expectation value of the kinetic energy as a function of the variational parameter α, $\langle\psi|T|\psi\rangle(\alpha)$. Due to spherical symmetry, only the radial part of the Laplacian $\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}$ needs to be considered and we first calculate the action of the Laplacian on the wavefunction ψ:

$$\begin{aligned}
T\psi &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}Ne^{-\alpha r^2} \\
&= -\frac{\hbar^2}{2m}N\frac{1}{r^2}\frac{d}{dr}r^2(-2\alpha r)e^{-\alpha r^2} \\
&= \frac{\hbar^2}{2m}2\alpha N\frac{1}{r^2}(3r^2 - 2\alpha r^4)e^{-\alpha r^2} \\
&= \frac{\hbar^2}{2m}2\alpha N(3 - 2\alpha r^2)e^{-\alpha r^2}
\end{aligned}$$

The expectation value can be now obtained by integrating $T\psi$ over entire space, considering

again spherical symmetry and integrating out the θ and ϕ coordinates to gain 4π:

$$
\begin{aligned}
\langle\psi|T|\psi\rangle(\alpha) =& 4\pi \int_0^\infty r^2 dr \, Ne^{-\alpha r^2} \frac{\hbar^2}{2m} 2\alpha N(3 - 2\alpha r^2)e^{-\alpha r^2} \\
=& 4\pi N^2 \frac{\hbar^2}{2m} 2\alpha \int_0^\infty dr (3r^2 - 2\alpha r^4)e^{-2\alpha r^2} \\
=& 4\pi \left(\frac{2\alpha}{\pi}\right)^{3/2} \frac{\hbar^2}{m}\alpha \left(3\sqrt{\frac{\pi}{2\alpha}}\frac{1}{8\alpha} - 2\alpha\sqrt{\frac{\pi}{2\alpha}}\frac{1}{8\alpha}\frac{3}{4\alpha}\right) \\
=& 8\alpha\frac{\hbar^2}{m}\left(\frac{3}{8} - \frac{3}{16}\right) \\
=& \frac{3\alpha\hbar^2}{2m}
\end{aligned}
$$

The expectation value of the potential energy is again straightforward to calculate in spherical coordinates

$$
\langle\psi|V|\psi\rangle(\alpha) = -4\pi \int_0^\infty r^2 dr \, N^2 e^{-2\alpha r^2}\frac{e^2}{4\pi\epsilon_0 r} = -4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{e^2}{4\pi\epsilon_0}\int_0^\infty dr \, r e^{-2\alpha r^2}
$$

We use a substitution $u = 2\alpha r^2, du = 4\alpha r dr$ to write

$$
= -4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{e^2}{4\pi\epsilon_0}\int_0^\infty du \frac{e^{-u}}{4\alpha} = -4\pi\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{e^2}{4\pi\epsilon_0}\frac{1}{4\alpha} = -2\sqrt{\frac{2\alpha}{\pi}}\frac{e^2}{4\pi\epsilon_0}.
$$

Collecting both results we find the energy dependence on the parameter α to be

$$
E(\alpha) = \frac{3\alpha\hbar^2}{2m} - 2\sqrt{\frac{2\alpha}{\pi}}\frac{e^2}{4\pi\epsilon_0}
$$

To find a stationary point of the dependence we compute the derivative

$$
\frac{dE(\alpha)}{d\alpha} = \frac{3\hbar^2}{2m} - \sqrt{\frac{2}{\alpha\pi}}\frac{e^2}{4\pi\epsilon_0}
$$

Setting the derivative equal to zero yields for $\sqrt{\alpha}$:

$$
\sqrt{\alpha} = \frac{2\sqrt{2}}{3}\frac{me^2}{4\pi\epsilon_0\hbar^2\sqrt{\pi}}
$$

The energy corresponding to this value of α is then

$$
\begin{aligned}
E =& \frac{3\hbar^2}{2m}\frac{8}{9}\frac{m^2 e^4}{(4\pi\epsilon_0)^2\hbar^4\pi} - 2\sqrt{\frac{2}{\pi}}\frac{e^2}{4\pi\epsilon_0}\frac{2\sqrt{2}}{3}\frac{me^2}{4\pi\epsilon_0\hbar^2\sqrt{\pi}} \\
=& \frac{4m}{3\pi\hbar^2}\left(\frac{e^4}{4\pi\epsilon_0}\right)^2 - \frac{8m}{3\pi\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \\
=& -\frac{4m}{3\pi\hbar^2}\left(\frac{e^4}{4\pi\epsilon_0}\right)^2
\end{aligned}
$$

The energy expression can be simplified considering that $\frac{m}{\hbar^2}\left(\frac{e^4}{4\pi\epsilon_0}\right)^2$ is one Hartree or two Rydbergs, the energy of the hydrogen $1s$ state. (We could also simply switch into atomic units which would eliminate all these constants.) We therefore gain

$$E = -\frac{4}{3\pi}[Ha] = -\frac{8}{3\pi}[Ry] \approx -0.8488[Ry]$$

The energy is above the correct result of one Rydberg, as expected.

Also note that at the optimal α, the kinetic energy contribution is minus one half of the potential energy. This is in agreement with the virial theorem for the potential of the hydrogen atom.

C. Particle in $r^{3/2}$ potential

A charged particle moves in a field of a spherically symmetric three dimensional potential $V = -\frac{g^2}{r^{3/2}}$, where $r^2 = x^2 + y^2 + z^2$. Using a testing function $\psi(r, \theta, \varphi) = \sqrt{\frac{k^3}{8\pi}}e^{-\frac{k}{2}r}$, where $k > 0$ is a parameter,

- validate that ψ is normalised;

- find variationally an approximate ground state energy.

Tha Laplace operator in three dimensions equals $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\Delta_{\theta,\varphi}}{r^2}$ and the Jacobi factor is $r^2\sin\theta$.

Solution:

For ψ to be normalised $\int d^3r\psi^*\psi$ needs to equal 1. The integral is

$$\begin{aligned}
\int d^3r\psi^*\psi &= \int d^3r\frac{k^3}{8\pi}e^{-kr} \\
&= \int_0^\infty dr\frac{k^3}{8\pi}4\pi r^2 e^{-kr} \\
&= \frac{k^3}{2}\int_0^\infty dr\, r^2 e^{-kr}.
\end{aligned}$$

We now use integration by parts to find

$$= k\int_0^\infty dr\, e^{-kr} = k\left[\frac{e^{-kr}}{-k}\right]_0^\infty = 1$$

The function is indeed normalised.

To obtain an upper estimate of the ground state energy, we find the expectation values of the kinetic and potential energies on the parameter k. First, we calculate the action of the Laplacian on the wavefunction

$$
\begin{aligned}
\Delta\psi &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}e^{-kr/2}\right) \\
&= -\frac{k}{2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 e^{-kr/2}\right) \\
&= -\frac{k}{2}\frac{1}{r^2}\left(2re^{-kr/2} - \frac{k}{2}r^2 e^{-kr/2}\right) \\
&= -\frac{ke^{-kr/2}}{r} + \frac{k^2}{4}e^{-kr/2}\,.
\end{aligned}
$$

We now use this result to find the expectation value of the kinetic energy

$$
\begin{aligned}
\langle\psi|T|\psi\rangle &= \frac{k^3}{8\pi}\int_0^\infty 4\pi r^2 e^{-kr/2}\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]e^{-kr/2}dr \\
&= \frac{k^3}{2}\int_0^\infty r^2 e^{-kr/2}\left[-\frac{\hbar^2}{2m}\left(-\frac{ke^{-kr/2}}{r} + \frac{k^2}{4}e^{-kr/2}\right)\right]dr \\
&= \frac{k^3}{2}\int_0^\infty \left(\frac{\hbar^2 k}{2m}re^{-kr} - \frac{\hbar^2 k^2}{8m}r^2 e^{-kr}\right)dr\,.
\end{aligned}
$$

Using

$$
\begin{aligned}
\int_0^\infty re^{-kr} &= \left[-\frac{(kr+1)e^{-kr}}{k^2}\right]_0^\infty = \frac{1}{k^2} \\
\int_0^\infty r^2 e^{-kr} &= \left[-\frac{(k^2r^2 + 2kr + 2)e^{-kr}}{k^3}\right]_0^\infty = \frac{2}{k^3}
\end{aligned}
$$

We obtain

$$
\begin{aligned}
\langle\psi|T|\psi\rangle &= \frac{k^3}{2}\left[\frac{\hbar^2 k}{2m}\frac{1}{k^2} - \frac{\hbar^2 k}{8m}\frac{2}{k^3}\right] \\
&= \frac{\hbar^2 k^2}{8m}\,.
\end{aligned}
$$

The expectation value of the potential energy can be calculated as

$$
\begin{aligned}
\langle\Phi|V|\Phi\rangle &= \frac{k^3}{8\pi}\int_0^\infty 4\pi r^2 e^{-kr/2}(-\frac{g^2}{r^{3/2}})e^{-kr/2}dr \\
&= -\frac{k^3}{2}\int_0^\infty g^2 r^{1/2}e^{-kr}dr\,.
\end{aligned}
$$

The integral can be evaluated as

$$
\int_0^\infty r^{1/2}e^{-kr} = \left[\frac{\sqrt{\pi}\,erf(\sqrt{kr})}{2k^{3/2}} - \frac{\sqrt{r}e^{-kr}}{k}\right]_0^\infty = \frac{\sqrt{\pi}}{2k^{3/2}}\,.
$$

So that

$$\langle \Phi|V|\Phi\rangle = -\frac{k^3}{2}g^2\frac{\sqrt{\pi}}{2k^{3/2}} = -g^2k^{3/2}\frac{\sqrt{\pi}}{4}\,.$$

Hence the energy depends on the parameter k as

$$E(k) = \frac{\hbar^2 k^2}{8m} - g^2 k^{3/2}\frac{\sqrt{\pi}}{4}\,.$$

Taking a derivative to find the extrema gives

$$\frac{\hbar^2 k}{4m} - 3g^2 k^{1/2}\frac{\sqrt{\pi}}{8} = 0$$

$$k^{1/2}\left(\frac{\hbar^2 k^{1/2}}{4m} - 3g^2\frac{\sqrt{\pi}}{8}\right) = 0\,.$$

The extrema at the limit $k = 0$ gives a constant wavefunction with energy equal to zero.

The extrema at

$$\frac{\hbar^2 k^{1/2}}{4m} - 3g^2\frac{\sqrt{\pi}}{8} = 0$$

$$k = \frac{9g^4 m^2 \pi}{4\hbar^4}$$

gives an energy

$$\begin{aligned}
E &= \frac{\hbar^2}{8m}\frac{81g^8 m^4 \pi^2}{16\hbar^8} - \frac{27g^6 m^3 \pi^{3/2}}{8\hbar^6}\frac{g^2\sqrt{\pi}}{4} \\
&= \frac{g^8 m^3 \pi^2}{\hbar^6}\left(\frac{3}{2}\right)^4\frac{1}{8} - \frac{g^8 m^3 \pi^2}{\hbar^6}\left(\frac{3}{2}\right)^3\frac{1}{4} \\
&= \frac{g^8 m^3 \pi^2}{\hbar^6}\left(\frac{3}{2}\right)^3\left[\frac{3}{16} - \frac{1}{4}\right] \\
&= -\frac{27g^8 m^3 \pi^2}{128\hbar^6}
\end{aligned}$$

which is our final estimate for the ground state energy of the system.

D.   No matrix element no fun

Assume a Hamiltonian of a system for two states ψ_a and ψ_b is

$$H = \begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix}$$

Show that no better solution can be found variationally than E_a and E_b.

Solution:

We form the trial wavefunction as $|\psi\rangle = cos\varphi|\psi_a\rangle + sin\varphi|\psi_b\rangle$. This is normalised. The energy expectation value using φ as a parameter is then

$$E = (cos\varphi\langle\psi_a| + sin\varphi\langle\psi_b|)H(cos\varphi|\psi_a\rangle + sin\varphi|\psi_b\rangle)$$
$$= cos^2\varphi\langle\psi_a|H|\psi_a\rangle + sin^2\varphi\langle\psi_b|H|\psi_b\rangle + cos\varphi sin\varphi\langle\psi_b|H|\psi_a\rangle + sin\varphi cos\varphi\langle\psi_a|H|\psi_b\rangle \,.$$

As the matrix element between the two functions $|\psi_a\rangle$ and $|\psi_b\rangle$ is zero, $\langle\psi_b|H|\psi_a\rangle = 0$, the last two terms drop out. The final expression for energy reads

$$E(\varphi) = cos^2\varphi\langle\psi_a|H|\psi_a\rangle + sin^2\varphi\langle\psi_b|H|\psi_b\rangle \,. \tag{1}$$

We find the extrema of $E(\varphi)$ by differentiating w.r.t. φ as

$$\frac{dE(\varphi)}{d\varphi} = -2cos\varphi sin\varphi\langle\psi_a|H|\psi_a\rangle + 2sin\varphi cos\varphi\langle\psi_b|H|\psi_b\rangle \,. \tag{2}$$

The expression is equal to zero if i) $sin\varphi = 0$ in which case $|\psi\rangle = |\psi_a\rangle$. ii) $cos\varphi = 0$ in which case $|\psi\rangle = |\psi_b\rangle$. iii) $H_{aa} = H_{bb}$ and the two vectors are degenerate with any combination giving identical energy. In the first two cases, clearly no mixing of the states is allowed.

E. Rotator with $cos^2\varphi$ perturbation

The wavefunctions of a rotator are $\psi_n = \frac{1}{\sqrt{2\pi}}exp(in\varphi)$ with $n \in Z$.

II. PERTURBATION THEORY

A. LHO with Ax^6 potential

The $V = \frac{1}{2}m\omega^2 x^2$ potential of linear harmonic oscillator changes to Ax^6, in the first order of the perturbation theory, calculate the energy of the ground state for the new potential.

Solution:

The original Hamiltonian reads

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

and in the perturbed Hamiltonian, $V = Ax^6$. The perturbing potential is then

$$V' = Ax^6 - \frac{1}{2}m\omega^2 x^2$$

In the first order of perturbation theory, we need to obtain the expectation value of V' for a given state. The ground state wavefunction is $\Psi = (\alpha/\pi)^{\frac{1}{4}} e^{\frac{\alpha x^2}{2}}$, with $\alpha = \frac{m\omega}{\hbar}$. The change of the energy of the ground state is then

$$\begin{aligned}
\Delta E_0 &= \langle 0|V'|0\rangle \\
&= \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} dx (-\frac{1}{2}m\omega) x^2 e^{-\alpha x^2} + \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} dx A x^6 e^{-\alpha x^2} \\
&= -\frac{1}{2}m\omega \sqrt{\frac{\alpha}{\pi}} \sqrt{\frac{\pi}{\alpha}} \frac{1}{2\alpha} + A \sqrt{\frac{\alpha}{\pi}} \frac{5}{2\alpha} \frac{3}{2\alpha} \frac{1}{2\alpha} \sqrt{\frac{\pi}{\alpha}} \\
&= -\frac{1}{2}m\omega \frac{\hbar}{2m\omega} + \frac{15A}{8\alpha^3} \\
&= -\frac{1}{4}\hbar\omega + \frac{15A}{8\alpha^3}
\end{aligned}$$

The expectation value of the original potential is half of the ground state energy, due to virial theorem.

B. LHO with doubled potential

Consider a particle with mass m moving in a field of harmonic potential with frequency ω. The frequency changes so that the potential is doubled. Show that the new ground state energy is exactly $E = \sqrt{2}E_0 = \frac{\sqrt{2}}{2}\hbar\omega$. Use perturbation theory to obtain the energy through third order.

Solution:

The Hamiltonian of the LHO is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \, ,$$

and the corresponding energies are $E_n = \hbar\omega(n + \frac{1}{2})$. When the potential is doubled, the frequency changes to a new frequency ω' which can be obtained as follows

$$\begin{aligned}
\frac{1}{2}m\omega'^2 &= 2 \cdot \frac{1}{2}m\omega^2 \\
\omega'^2 &= 2\omega^2 \\
\omega' &= \sqrt{2}\omega \, .
\end{aligned}$$

We see that the new frequency is $\sqrt{2}$ times the original one. The energies for the new potential are then $E_n' = \hbar\omega'(n + \frac{1}{2}) = \sqrt{2}\hbar\omega(n + \frac{1}{2})$.

The change of the energy in the first order of parturbation theory is given by $\Delta E^1 = \langle \psi | V' | \psi \rangle$. For the ground state this is

$$\begin{aligned}\Delta E_0^1 &= \langle 0 | V' | 0 \rangle \\ &= \langle 0 | \frac{1}{2} m\omega^2 x^2 | 0 \rangle \\ &= \frac{1}{4} \hbar\omega \,,\end{aligned}$$

where in the last step we used the virial theorem which gives for LHO that the mean value of the potential energy is one half of the total energy.

Alternatively, the expectation value can be evaluated using the the raising (a) and lowering a^+ operators for LHO and considering $x = \frac{\alpha}{\sqrt{2}}(a + a^+)$. For x^2 we than obtain

$$x^2 = \frac{\alpha^2}{2}(a + a^+)(a + a^+) = \frac{\alpha^2}{2}(a^2 + a^{+2} + aa^+ + a^+a) = \frac{\alpha^2}{2}(a^2 + a^{+2} + 2a^+a + 1)$$

With $\alpha = \sqrt{\frac{\hbar}{m\omega}}$ The expectation value of the perturbing potential $V' = \frac{1}{2} m\omega^2 x^2$ is then

$$\begin{aligned}\langle 0 | V' | 0 \rangle &= \frac{1}{2} m\omega^2 \frac{\hbar}{2m\omega} \langle 0 | a^2 + a^{+2} + 2a^+a + 1 | 0 \rangle \\ &= \frac{1}{4} \hbar\omega \langle 0 | 1 | 0 \rangle \\ &= \frac{1}{4} \hbar\omega \,.\end{aligned}$$

In the last step we used the fact that the terms $\langle 0 | a^2 | 0 \rangle$ and $\langle 0 | a^{+2} | 0 \rangle$ are zero as they result in a different state on the right and on the left. Moreover, the term $\langle 0 | a^+a | 0 \rangle$ is zero as $a | 0 \rangle = 0$, so that only the identity operator remains. The final result is then identical to the one obtained from the knowledge of the virial theorem. Finally, an explicit integration could be performed as well to obtain the result.

Therefore, in the first order of perturbation theory, we find that the estimated value of the ground state energy for the perturbed system is

$$E_0^1 = \frac{1}{2} \hbar\omega + \frac{1}{4} \hbar\omega = \frac{3}{4} \hbar\omega \,. \tag{3}$$

This is above the exact result of $\frac{2\sqrt{2}}{4} \hbar\omega$.

The correction to the energy in the second order is

$$\Delta E_0^2 = \sum_{j \neq 0}^{\infty} \frac{|\langle j | V' | 0 \rangle|^2}{\epsilon_0 - \epsilon_j} \,.$$

For the perturbation $x^2 \sim a^2 + a^{+2} + 2a^+ a + 1$, only the matrix element between the ground state and the second excited state will be non-zero, as a result of the action of the a^{+2} operator. Therefore, the expression for the energy correction simplifies to

$$\Delta E_0^2 = \frac{m^2 \omega^4}{4} \frac{\alpha^4}{4} \frac{|\langle 2|a^{+2}|0\rangle|^2}{\epsilon_0 - \epsilon_2} \, ,$$

where the first fraction comes from the square of $\frac{1}{2}m\omega^2$ and the second fraction from the square of the $\frac{\alpha^2}{2}$ coefficient. Using $\alpha^2 = \frac{\hbar}{m\omega}$, $\epsilon_2 = \frac{5}{2}\hbar\omega$, and $a^+|n\rangle = \sqrt{n+1}|n+1\rangle$ we find

$$\begin{aligned}
\Delta E_0^2 &= \frac{m^2 \omega^4}{4} \frac{\hbar^2}{4m^2\omega^2} \frac{|\sqrt{2}|^2}{\frac{1}{2}\hbar\omega - \frac{5}{2}\hbar\omega} \\
&= \frac{\omega^2 \hbar^2}{16} \frac{2}{-2\hbar\omega} \\
&= -\frac{\hbar\omega}{16} \, .
\end{aligned}$$

As expected for ground state energy, the second order correction is negative.

The correction to within second order is then

$$E_0^2 = \frac{1}{2}\hbar\omega + \frac{1}{4}\hbar\omega - \frac{\hbar\omega}{16} = \frac{1}{2}\hbar\omega \cdot \frac{11}{8} \, . \tag{4}$$

The factor $\frac{11}{8} = 1.375$ is now closer to the $\sqrt{2} \approx 1.414$.

The correction to the ground state energy in third order can be written as

$$\begin{aligned}
\Delta E_0^3 = \sum_{j \neq 0} \sum_{k \neq 0} &\frac{\langle 0|V'|k\rangle\langle k|V'|j\rangle\langle j|V'|0\rangle}{(\epsilon_0 - \epsilon_k)(\epsilon_0 - \epsilon_j)} \\
&- \langle 0|V'|0\rangle \sum_{j \neq 0} \frac{|\langle j|V'|0\rangle|^2}{(\epsilon_0 - \epsilon_j)^2} \, .
\end{aligned}$$

For a matrix element of the x^2 perturbation to be non-zero, the quantum number needs to differ by two (in both directions), or needs to stay constant. Considering that neither j nor k can be the ground state in the first expression, a non-zero contribution comes only from $j = k = 2$ in the first expression. In the second expression, $j = 2$, as in the second order. Explicit evaluation of the terms gives $\frac{5}{128}\hbar\omega$ for the first term and $\frac{-\hbar\omega}{128}$ for the latter. Overall, third order contributes $\frac{1}{32}\hbar\omega$ to the energy, giving

$$E_0^3 = 1.4375 \cdot \frac{1}{2}\hbar\omega \, . \tag{5}$$

Comparing the results to sums for $\sqrt{2}$, we find that the formula

$$\sqrt{2} = \sum_{k=0}^{\infty} (-1)^{k+1} \frac{(2k-3)!!}{(2k)!!} \tag{6}$$

$$= 1 + \frac{1}{2} - \frac{1}{2 \cdot 4} + \frac{1 \cdot 3}{2 \cdot 4 \cdot 6} - \frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6 \cdot 8} + \ldots \tag{7}$$

gives identical coefficients to those we found using perturbation theory. It is then very likely that the subsequent orders of perturbation theory would follow the series.

C. Free particle with Dirac δ

Consider a free particle within periodic boundary conditions on an interval $(0, L)$. What are the wavefunctions, energies, and degeneracies of the states? A perturbing potential of the form $V' = A\delta(x - L/2)$ (periodically repeated) is added. What are the matrix elements between any pair states for the perturbing potential? What is the correction to the energy level for the ground state in the first and second order of perturbation theory? What are the energies and wavefunctions of the first excited states within the first order of perturbation theory? What is the first order change of the wavefunction of the ground state?

Solution:

The states of a particle within periodic boundary conditions are $\frac{\Psi_n = \frac{1}{\sqrt{L}} exp(2\pi i n x}{L)}$, where L is the length of the box and n is integer. For constant potential equal to zero, only kinetic energy contributes to the total energy, so that $E_n = \frac{2\hbar^2\pi^2}{mL^2}n^2$. The ground state is non-degenerate and all the excited states are twice degenerate, as the states with both positive and negative n occur.

The matrix elements of the perturbing potential are

$$\langle m|V'|n\rangle = \frac{A}{L} \int_0^L e^{-\frac{2\pi i}{L}mx} \delta(x - \frac{L}{2}) e^{\frac{2\pi i}{L}nx}$$

$$= \frac{A}{L} e^{\frac{2\pi i}{L}\frac{L}{2}(n-m)}$$

$$= \frac{A}{L} e^{i\pi(n-m)} .$$

The matrix element is thus $\frac{A}{L}$ for pairs of states with $(n-m)$ even and $-\frac{A}{L}$ for $(n-m)$ odd. The first order correction to the energy of the ground state $n = m = 0$ is then $\Delta E_0^1 = \frac{A}{L}$. This means that for $A > 0$ the potential is repulsive and the energy increases while for $A < 0$, the potential is attractive and the energy is lowered.

In the second order we need to evaluate

$$\Delta E_0^{(2)} = \sum_{j \in \{Z-0\}} \frac{|\langle j|V'|0\rangle|^2}{\epsilon_0 - \epsilon_j} \, .$$

In this case the matrix elements of the perturbation between the ground state and the excited states are all non-zero. Fortunately, they are all $\pm \frac{A}{L}$ so that their squares are simply $\frac{A^2}{L^2}$. The energy of the unperturbed ground state is zero ($\epsilon_0 = 0$) and the energies of the excited states are $E_n = \frac{2\hbar^2 \pi^2}{mL^2} n^2$. We thus find for the correction

$$\Delta E_0^{(2)} = \sum_{j \in \{Z-0\}} \frac{\frac{A^2}{L^2}}{0 - \frac{2\hbar^2 \pi^2 n^2}{mL^2}}$$

$$= -\frac{A^2 m}{2\hbar^2 \pi^2} \sum_{j \in \{Z-0\}} \frac{1}{j^2}$$

$$= -\frac{A^2 m}{\hbar^2 \pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \, .$$

The summation over inverse squares is known as the "Basel problem", posed in 1644 and was first derived by Leonhard Euler almost a hundred years later. The sum equals $\pi^2/6$. The final correction is thus

$$\Delta E_0^{(2)} = -\frac{A^2 m}{\hbar^2 \pi^2} \frac{\pi^2}{6}$$

$$= -\frac{A^2 m}{6\hbar^2}$$

As expected for the second order energy correction to the ground state, $\Delta E_0^{(2)}$ is negative and always lowers the energy.

The excited states are twice degenerate, we therefore need to diagonalise the partial Hamiltonian of the perturbation corresponding to these states to find their energies in the first order of perturbation theory. The partial Hamiltonian contains the diagonal matrix elements $\langle n|V'|n\rangle$ as well as the elements of type $\langle n|V'|-n\rangle$. In both cases, the matrix elements are A/L and the matrix to diagonalise is

$$V'_{\text{sub}} = \frac{A}{L} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

The eigenvalues of this matrix are 0, for the state $\frac{1}{\sqrt{2}}(|n\rangle - |-n\rangle)$, and $\frac{2A}{L}$ for the state $\frac{1}{\sqrt{2}}(|n\rangle + |-n\rangle)$. This result can be simply explained considering that

$$\frac{1}{\sqrt{2}}(|n\rangle - |-n\rangle) = i\sqrt{\frac{2}{L}} \sin(2\pi n x/L) \, ,$$

which equals zero for $x = L/2$ and thus is not affected by the potential. The second state is then

$$\frac{1}{\sqrt{2}}(|n\rangle + |-n\rangle) = \sqrt{\frac{2}{L}}cos(2\pi nx/L)\,,$$

which has a non-zero value for $x = L/2$.

We now calculate the correction to the ground state wavefunction. The first order correction reads

$$|i^{(1)}\rangle = |i^{(0)}\rangle + \sum_{j\in\{Z-i\}} \frac{|j\rangle\langle j|V'|i\rangle}{\epsilon_i - \epsilon_j}\,.$$

Inserting the matrix element of the perturbation

$$|i^{(1)}\rangle = |i^{(0)}\rangle + \sum_{j\in\{Z-i\}} \frac{|j\rangle\frac{A}{L}e^{i\pi(j-i)}}{\epsilon_i - \epsilon_j}\,.$$

For the ground state $i = 0$ and we obtain

$$|0^{(1)}\rangle = \frac{1}{\sqrt{L}} + \sum_{j\in\{Z-0\}} \frac{\frac{1}{\sqrt{L}}e^{\frac{2\pi ijx}{L}}\frac{A}{L}e^{i\pi j}}{-\frac{2\hbar^2\pi^2 j^2}{mL^2}}$$

$$= \frac{1}{\sqrt{L}} - \frac{mL^2}{2\hbar^2\pi^2}\frac{1}{\sqrt{L}}\frac{A}{L} \sum_{j\in\{Z-0\}} \frac{e^{\frac{2\pi ijx}{L}}e^{i\pi j}}{j^2}$$

$$= \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{2\hbar^2\pi^2} \sum_{j\in\{Z-0\}} \frac{e^{\frac{2\pi ijx}{L}}e^{i\pi j}}{j^2}\,.$$

We now change the summation from all integers, except for zero, to summation over natural numbers (1 to ∞), putting the $-j$ term together with the $+j$ term

$$|0^{(1)}\rangle = \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{2\hbar^2\pi^2} \sum_{j=1}^{\infty} \frac{e^{i\pi j}[e^{\frac{2\pi ijx}{L}} + e^{-\frac{2\pi ijx}{L}}]}{j^2} = \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{\hbar^2\pi^2} \sum_{j=1}^{\infty} \frac{(-1)^j cos(\frac{2\pi jx}{L})}{j^2}\,.$$

We see that all excited states contribute to the first order correction to the wavefunction.

For the interesting point of $x = L/2$ we obtain

$$\psi_0^{(1)}(L/2) = \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{\hbar^2\pi^2} \sum_{j=1}^{\infty} \frac{(-1)^j cos(\frac{2\pi jL}{2L})}{j^2}$$

$$= \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{\hbar^2\pi^2} \sum_{j=1}^{\infty} \frac{(-1)^j cos(\pi j)}{j^2}\,.$$

Since $cos(\pi j) = (-1)^j$, we get

$$
\begin{aligned}
\psi_0^{(1)}(L/2) &= \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{\hbar^2\pi^2} \sum_{j=1}^{\infty} \frac{(-1)^{2j}}{j^2} \\
&= \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{\hbar^2\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \\
&= \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{\hbar^2\pi^2} \frac{\pi^2}{6} \\
&= \frac{1}{\sqrt{L}} - \frac{mA\sqrt{L}}{6\hbar^2} \; .
\end{aligned}
$$

The sign of the correction is correct – when $A > 0$, a repulsive potential is present and the density will be reduced, for the opposite case of an attractive potential, the density will increase.

Interestingly, one can see that the second derivative becomes infinite. This agrees with the fact that for the δ potential, the exact wavefunction contains a jump in the derivative in the point of the potential. We try to model this potential with smooth functions which can reach the exact result only in the infinite limit. An exactly the same problem of slow convergence of the wavefunction with the number of excited states considered is encountered when using perturbation theory for the many-electron problem in atoms, molecules, and solids.

D. LHO with Ax^2y^2 perturbation

A particle with mass m moves in the x-y plane in a 2D isotropic linear harmonic oscillator potential with a frequency ω and centered at origin. The particle is subject to an additional perturbing potential of the form $V' = Ax^2y^2$. What is the energy of the ground state to within second order perturbation theory? What are the energies of the first and second excited states in the first order of perturbation theory?

Solution:

The unperturbed Hamiltonian is

$$
H_0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2}m\omega(x^2 + y^2),
$$

the corresponding eigenstates are $\psi_n(x) \otimes \psi_m(y) = |nm\rangle$ and the eigenenergies $E_{nm} = \hbar\omega(n + m + 1)$.

The corrections to the original energies can be simply evaluated when the perturbing potential is rewritten using the lowering and raising operators for the LHO. As $x = \frac{\alpha}{\sqrt{2}}(a + a^+)$, we obtain

$$V' = A\frac{\alpha^4}{4}(a^2 + a^{+2} + 2a^+a + 1) \otimes (b^2 + b^{+2} + 2b^+b + 1),$$

where a acts in the x space and b in the y space. We see that non-zero matrix elements between different states occur when the quantum number n is either lowered or decreased by two or stays constant. The same (but independent) requirement holds for the quantum number m. This means that, for example, the diagonal matrix elements will be non-zero as both indices stay constant (e.g., matrix elements of the type $\langle nm|V'|nm\rangle$).

The first order correction to the ground state energy is obtained as the matrix element of the perturbation

$$\begin{aligned}
\langle 00|V'|00\rangle =& A\frac{\alpha^4}{4}\langle 00(a^2 + a^{+2} + 2a^+a + 1) \otimes (b^2 + b^{+2} + 2b^+b + 1)|00\rangle \\
=& A\frac{\alpha^4}{4}\langle 0|2a^+a + 1|0\rangle \otimes \langle 0|2b^+b + 1|0\rangle \\
=& A\frac{\alpha^4}{4}\langle 0|1|0\rangle \otimes \langle 0|1|0\rangle \\
=& A\frac{\alpha^4}{4},
\end{aligned}$$

where we used that $a|0\rangle = 0$ and that the matrix elements of the squares of lowering or raising operators are zero.

In the second order correction to the ground state energy, only states $|20\rangle$, $|02\rangle$, and $|22\rangle$ will contribute as for V' all the other states have zero matrix elements with the ground state. The contributions are

$$\begin{aligned}
\Delta E(|20\rangle) =& \frac{|\langle 00|V'|20\rangle|^2}{\epsilon_0 - \epsilon_{20}} \\
=& A^2\frac{\alpha^8}{16}\frac{|\langle 00|a^2 \otimes (2b^+b + 1)|20\rangle|^2}{\hbar\omega - 3\hbar\omega} \\
=& A^2\frac{\alpha^8}{16}\frac{(\sqrt{2} \cdot 1)^2}{-2\hbar\omega} \\
=& -A^2\frac{\alpha^8}{16\hbar\omega},
\end{aligned}$$

where we wrote only the relevant operators of the perturbation on the second line. The contribution of the state $|02\rangle$ will be identical.

The correction to the energy from the state $|22\rangle$ is

$$
\begin{aligned}
\Delta E(|22\rangle) =& \frac{|\langle 00|V'|22\rangle|^2}{\epsilon_0 - \epsilon_{22}} \\
=& A^2 \frac{\alpha^8}{16} \frac{|\langle 00|a^2 \otimes b^2|22\rangle|^2}{\hbar\omega - 5\hbar\omega} \\
=& A^2 \frac{\alpha^8}{16} \frac{(\sqrt{2} \cdot \sqrt{2})^2}{-4\hbar\omega} \\
=& -A^2 \frac{\alpha^8}{16\hbar\omega} \,,
\end{aligned}
$$

Hence the same correction is found also here, so that the total ground state energy through second order is

$$
E_{00}^{(2)} = \hbar\omega + A\frac{\alpha^4}{4} - 3A^2 \frac{\alpha^8}{16\hbar\omega} \,.
$$

There are two first excited states, namely $|10\rangle$ and $|01\rangle$, each with energy $2\hbar\omega$. For degenerate states we need to diagonalise the partial Hamiltonian within the subspace of the degenerate states. However, in this case one can see that $\langle 10|V'|01\rangle = 0$ since each quantum number changes by one and such states are not coupled by the perturbation. Therefore, the energies of both the states will remain degenerate and will shift by $\langle 10|V'|10\rangle$, which is

$$
\begin{aligned}
\langle 10|V'|10\rangle =& A\frac{\alpha^4}{4}\langle 10|(a^2 + a^{+2} + 2a^+a + 1) \otimes (b^2 + b^{+2} + 2b^+b + 1)|10\rangle \\
=& A\frac{\alpha^4}{4}\langle 1|2a^+a + 1|1\rangle \otimes \langle 0|2b^+b + 1|0\rangle \\
=& A\frac{\alpha^4}{4}\langle 1|2a^+a + 1|1\rangle \otimes \langle 0|1|0\rangle \\
=& 3A\frac{\alpha^4}{4} \,.
\end{aligned}
$$

There are three excited states, $|20\rangle$, $|02\rangle$, and $|11\rangle$. The state $|11\rangle$ has zero matrix elements of the perturbation with the other two states and will shift by

$$
\begin{aligned}
\langle 11|V'|11\rangle =& A\frac{\alpha^4}{4}\langle 11|(a^2 + a^{+2} + 2a^+a + 1) \otimes (b^2 + b^{+2} + 2b^+b + 1)|11\rangle \\
=& A\frac{\alpha^4}{4}\langle 1|2a^+a + 1|1\rangle \otimes \langle 1|2b^+b + 1|1\rangle \\
=& A\frac{\alpha^4}{4}3 \cdot 3 \\
=& 9A\frac{\alpha^4}{4} \,.
\end{aligned}
$$

The matrix element of the perturbation is non-zero between states $|20\rangle$ and $|02\rangle$ so we need to calculate and diagonalise the partial Hamiltonian. For this, we need $\langle 20|V'|20\rangle$ which

will be identical to $\langle 02|V'|02\rangle$ due to the symmetry of the perturbation, and the coupling element $\langle 20|V'|02\rangle$, which is again identical to the conjugate $\langle 02|V'|20\rangle$. We obtain

$$
\begin{aligned}
\langle 20|V'|20\rangle =& A\frac{\alpha^4}{4}\langle 20(a^2 + a^{+2} + 2a^+a + 1) \otimes (b^2 + b^{+2} + 2b^+b + 1)|20\rangle \\
=& A\frac{\alpha^4}{4}\langle 2|2a^+a + 1|2\rangle \otimes \langle 0|1|0\rangle \\
=& A\frac{\alpha^4}{4}5 \cdot 1 \\
=& 5A\frac{\alpha^4}{4} ,
\end{aligned}
$$

for the diagonal part and

$$
\begin{aligned}
\langle 20|V'|02\rangle =& A\frac{\alpha^4}{4}\langle 20(a^2 + a^{+2} + 2a^+a + 1) \otimes (b^2 + b^{+2} + 2b^+b + 1)|02\rangle \\
=& A\frac{\alpha^4}{4}\langle 2|a^{+2}|0\rangle \otimes \langle 0|b^2|2\rangle \\
=& A\frac{\alpha^4}{4}\sqrt{2} \cdot \sqrt{2} \\
=& A\frac{\alpha^4}{2} .
\end{aligned}
$$

for the coupling element. The partial Hamiltonian is then

$$
H_{02,20} = A\frac{\alpha^4}{4}\begin{pmatrix} 5 & 2 \\ 2 & 5 \end{pmatrix} ,
$$

which has eigenvalues $(5 \pm 2)A\frac{\alpha^4}{4}$. For $A > 0$, the lower energy state with $E = 3A\frac{\alpha^4}{4}$ corresponds to a combination $\frac{1}{\sqrt{2}}(|20\rangle - |02\rangle)$ and the higher energy state with $E = 7A\frac{\alpha^4}{4}$ is the combination $\frac{1}{\sqrt{2}}(|20\rangle + |02\rangle)$.

III.   ANGULAR MOMENTUM

A.   Lim 3004

Calculate the expectation values of L_x and L_x^2 for a state with angular momentum $l\hbar$ and a projection onto the z axis $m\hbar$.

Solution:

The expectation value of L_x can be obtained using the commutation relations for components of angular momentum: $i\hbar L_x = [L_y, L_z]$. Hence

$$
\langle L_x\rangle = \langle lm|\frac{1}{i\hbar}[L_y, L_z]|lm\rangle = \frac{1}{i\hbar}\langle lm|L_yL_z - L_zL_y|lm\rangle
$$

We now use $L_z|lm\rangle = \hbar m|lm\rangle$ (and its conjugate) to find

$$\langle L_x\rangle = \frac{1}{i\hbar}\langle lm|m\hbar L_y|lm\rangle - \frac{1}{i\hbar}\langle lm|m\hbar L_y|lm\rangle = 0\,.$$

Alternatively, we can make use of the rising and lowering operators for angular momentum

$$L_+ = L_x + iL_y \qquad L_- = L_x - iL_y\,.$$

Which gives $L_x = \frac{1}{2}(L_+ + L_-)$. As

$$L_\pm|lm\rangle = \hbar\sqrt{l(l+1) - m(m\pm 1)}|lm\pm 1\rangle\,,$$

we obtain

$$\begin{aligned}
\langle lm|L_x|lm\rangle &= \frac{1}{2}\hbar\sqrt{l(l+1) - m(m+1)}\langle lm|lm+1\rangle \\
&+ \frac{1}{2}\hbar\sqrt{l(l+1) - m(m-1)}\langle lm|lm-1\rangle \\
&= 0\,,
\end{aligned}$$

as the basis of the $|lm\rangle$ states is orthonormal.

The expectation value of the square of the L_x operator can be obtained using the operator of the magnitude of the momentum L^2 and of the projection into the z axis. As $L^2 = L_x^2 + L_y^2 + L_z^2$ and $\langle L_x^2\rangle = \langle L_y^2\rangle$, due to the symmetry of the problem, the expectation value is $\langle L_x^2\rangle = \frac{1}{2}\langle(L^2 - L_z^2)\rangle$. Using $L^2|lm\rangle = l(l+1)\hbar^2|lm\rangle$ and $L_z|lm\rangle = \hbar m|lm\rangle$, we obtain $\langle L_x^2\rangle = \frac{1}{2}\hbar^2(l(l+1) - m^2)$.

Using the raising and lowering operators, we have

$$L_x^2 = \frac{1}{4}(L_+ + L_-)(L_+ + L_-) = \frac{1}{4}(L_+L_+ + L_-L_- + L_-L_+ + L_+L_-)$$

The expectation value of the squares of the raising or lowering operators is zero (as $\langle lm|L_+^2|lm\rangle = c\langle lm|lm+2\rangle = 0$) and only the mixed terms remain. They can be eval-

uated as

$$
\begin{aligned}
\langle L_x^2 \rangle =& \frac{1}{4} \langle lm|L_-L_+ + L_+L_-|lm \rangle \\
=& \frac{1}{4}\hbar \langle lm|L_-\sqrt{l(l+1)-m(m+1)}|lm+1 \rangle + \frac{1}{4}\hbar \langle lm|L_+\sqrt{l(l+1)-m(m-1)}|lm-1 \rangle \\
=& \frac{1}{4}\hbar^2 \langle lm|\sqrt{l(l+1)-(m+1)(m+1-1)}\sqrt{l(l+1)-m(m+1)}|lm \rangle \\
& + \frac{1}{4}\hbar^2 \langle lm|\sqrt{l(l+1)-(m-1)(m-1+1)}\sqrt{l(l+1)-m(m-1)}|lm \rangle \\
=& \frac{1}{4}\hbar^2(l(l+1)-m(m+1)) + \frac{1}{4}\hbar^2(l(l+1)-m(m-1)) \\
=& \frac{1}{4}\hbar^2(2l(l+1)-m(m+1)-m(m-1)) \\
=& \frac{1}{2}\hbar^2(l(l+1)-m^2) \,.
\end{aligned}
$$

Which agrees with the previous result.

B. Lim 3007

A particle with spin $S = 1$ is in a state with an angular momentum of $L = 2$. A spin-orbit Hamiltonian

$$
H = AL \cdot S
$$

describes the interaction between the particles. What are the possible energies and their degeneracies for this system.

Solution: The spin-orbit Hamiltonian does not commute with individual projections of the spin and angular momentum, i.e. $[L_z, L \cdot S] \neq 0$ and $[S_z, L \cdot S] \neq 0$. The Hamiltonian is, however, diagonal in the basis of the total momentum $J = L + S$ and its projections $J_z = L_z + S_z$.

The Hamiltonian can be rewritten using the operator of the magnitude of the total momentum $J^2 = L^2 + S^2 + 2L \cdot S$, from which we find

$$
L \cdot S = \frac{1}{2}(J^2 - L^2 - S^2) \,.
$$

The magnitude of the ($L = 2$) orbital momentum is $L^2|lm\rangle = l(l+1)\hbar^2|lm\rangle = 6\hbar^2|lm\rangle$ and for spin ($S = 1$) we have $S^2|ss_z\rangle = s(s+1)\hbar^2|ss_z\rangle = 2\hbar^2|ss_z\rangle$ and are thus identical for all the states.

The rules of combination of angular momenta give possible values for the total momentum $J = L + S, \ldots, |L - S|$. Therefore, for $L = 2$ and $S = 1$ we have $J = 3, 2, 1$. The magnitude

of the total momentum is $J^2|JJ_zLS\rangle = J(J+1)\hbar^2|JJ_zLS\rangle$, which, for the possible values of J gives $12\hbar^2$, $6\hbar^2$, and $2\hbar^2$, respectively. As the expectation values of the Hamiltonian are

$$\langle H\rangle = \langle JJ_zLS|\frac{A}{2}(J^2 - L^2 - S^2)|JJ_zLS\rangle\,,$$

We get

$$E(J = 3) = 2A\hbar^2$$
$$E(J = 2) = -A\hbar^2$$
$$E(J = 1) = -3A\hbar^2$$

which are 7, 5, and 3-fold degenerate, respectively.

C. Two spins – Lim 3034

Consider a system with two non-interacting spins. The first is in a state $s_z^A = +1/2$, the second in a state $s_x^B = +1/2$. What's the probability that the total spin is zero?

Solution:

Two particles with spin one half lead to total spin one with three-fold degeneracy and a non-degenerate spin zero state. For the total spin equal to zero, the state is (taking z as the quantisation coordinate)

$$|S = 0, S_z = 0\rangle = \frac{1}{\sqrt{(2)}}(|\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle)\,.$$

To be able to project on this state, we need to transform the $s_x^B = +1/2$ state into the s_z^B basis. The representation of the s_x^B states can be found by diagonalisation of the s_x operator matrix

$$s_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{8}$$

The eigenvalues are $\pm 1\hbar/2$ and the states are $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ for the $+\hbar/2$ state and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$ for the $-\hbar/2$ state. That is, $|s_x = +1/2\rangle = \frac{1}{\sqrt{2}}(|s_z = +1/2\rangle + |s_z = -1/2\rangle)$. Therefore,

$$|s_z^A = +1/2, s_x^B = +1/2\rangle = \frac{1}{\sqrt{2}}(|s_z^A = +1/2, s_z^B = +1/2\rangle + |s_z^A = +1/2, s_z^B = -1/2\rangle)\,.$$

The projection on the zero spin state is then (in a short-hand notation)

$$\langle 00|s_z^A = +1/2, s_x^B = +1/2\rangle = \frac{1}{2}\left(\langle\uparrow_A\downarrow_B| - \langle\downarrow_A\uparrow_B|\right)\left(|\uparrow_A\uparrow_B\rangle + |\uparrow_A\downarrow_B\rangle\right)$$

$$= \frac{1}{2}\left(\langle\uparrow_A\downarrow_B|\uparrow_A\uparrow_B\rangle + \langle\uparrow_A\downarrow_B|\uparrow_A\downarrow_B\rangle - \langle\downarrow_A\uparrow_B|\uparrow_A\uparrow_B\rangle - \langle\downarrow_A\uparrow_B|\uparrow_A\downarrow_B\rangle\right)$$

$$= \frac{1}{2}(0 + 1 + 0 + 0) = \frac{1}{2}$$

$$(9)$$

The probability is

$$|\langle 00|s_z^A = +1/2, s_x^B = +1/2\rangle|^2 = \frac{1}{4}.$$

D. Lim 3017

An electron is prepared with projection of the spin $+\hbar/2$ along the z axis.

- What are the possible results of measurement of spin along the x axis?

- What is the probability of finding these results?

- If we measure the spin along axis restricted to the $x - z$ plane and rotated by an angle θ from the z axis, what are the probabilities of measuring the different results?

- What is the expectation value of spin measured along the rotated axis, given the initial projection along z?

Solution:

The measured electron spin will be $\pm\hbar/2$ along any axis. This can be shown by finding the eigenvalues of the s_x operator that describes the act of measuring the spin along x axis. Its eigenvalues are then the only possible results of measuring the spin (given an isolated system). We find the eigenvalues by diagonalising the matrix representation of the s_x operator in the basis of the states corresponding to measurement along the z axis. The s_x operator is given as

$$s_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

The eigenvalues are found by calculating the determinant of

$$\frac{\hbar}{2}\begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} = \lambda^2 - 1,$$

therefore the eigenvalues are indeed $\lambda = \pm\hbar/2$. The eigenvector corresponding to $\lambda = \hbar/2$ is $\frac{1}{\sqrt{2}}\binom{1}{1}$ and the eigenvector corresponding to $\lambda = -\hbar/2$ is $\frac{1}{\sqrt{2}}\binom{1}{-1}$.

E.   Spin-spin Hamiltonian

Two particles (A and B) with spin $1/2$ interact via Hamiltonian $H = Js^A \cdot s^B$. Find the eigenenergies of the Hamiltonian by rewriting it using the operators of the magnitudes of the spin.

Solution:

The problem is analogous to the problem of spin-orbit interaction. The dot product in the Hamiltonian does not commute with the operators of the projections of the individual spins into the z axis. We therefore introduce the total spin $S = s^A \otimes 1_B + 1_A \otimes s^B$ and its projection $S_z = s_z^A \otimes 1_B + 1_A \otimes s_z^B$, which commute with the Hamiltonian. By the rules of combination of angular momenta the total spin can be either $S = \frac{1}{2} + \frac{1}{2} = 1$ or $S = \frac{1}{2} - \frac{1}{2} = 0$. In the first case, three projections are possible, in the latter, only one.

To find the new eigenvalues we rewrite the dot product using the operator of the magnitude of the total spin

$$S^2 = (s_A + s_B)^2 = s_A^2 \otimes 1_B + 1_A \otimes s_B^2 + 2s^A \cdot s^B. \tag{10}$$

Hence

$$s^A \cdot s^B = \frac{1}{2}(S^2 - s_A^2 \otimes 1_B - 1_A \otimes s_B^2). \tag{11}$$

The action of an operator of the magnitude of the spin is $s^2|ss_z\rangle = \hbar^2 s(s+1)|ss_z\rangle$. For particles with spin $s = \frac{1}{2}$, we obtain $\frac{3}{4}\hbar^2$. For the triplet states with total spin $S = 1$, we get $2\hbar^2$ and for the singlet state with spin $S = 0$ we get 0.

The energies are then for triplet

$$E(\text{T}) = \frac{J}{2}(2\hbar^2 - \frac{3}{4}\hbar^2 - \frac{3}{4}\hbar^2) = \frac{J}{4}\hbar^2 \tag{12}$$

and for the singlet state

$$E(\text{S}) = \frac{J}{2}(0 - \frac{3}{4}\hbar^2 - \frac{3}{4}\hbar^2) = -\frac{3J}{4}\hbar^2. \tag{13}$$

This agrees with the results obtained by exact diagonalisation.

F. Spin-spin Hamiltonian in matrix representation

Two particles (A and B) with spin 1/2 interact via Hamiltonian $H = J s^A \cdot s^B$. Write the matrix representation of the Hamiltonian in the direct basis. Find the eigenvectors and eigenvalues of the Hamiltonian.

Solution:

The Hamiltonian reads $A s^A \cdot s^B$, where the dot product stands for

$$s^A \cdot s^B = s_x^A \otimes s_x^B + s_z^A \otimes s_z^B + s_z^A \otimes s_z^B .$$

The matrix representation of the spin operators (s_x etc.) in the standard quantisation along z axis uses the Pauli matrices

$$s_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$s_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$s_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The basis functions are spin up and down along the z axis: $| \uparrow \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $| \downarrow \rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Calculating the expectation values of the spin components using these vectors gives zeros for the x and y components and either $\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$ for the z component, as expected.

The Hamiltonian is written as a direct product of the spin matrices, it can be thus written as a 4×4 matrix. We will go from the direct product of two 2×2 matrices to the 4×4 matrix using the following scheme:

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} \otimes \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} = \begin{pmatrix} A\alpha & A\beta & B\alpha & B\beta \\ A\gamma & A\delta & B\gamma & B\delta \\ C\alpha & C\beta & D\alpha & D\beta \\ C\gamma & C\delta & D\gamma & D\delta \end{pmatrix} \tag{14}$$

This corresponds to a basis set $| \uparrow\uparrow \rangle$, $| \uparrow\downarrow \rangle$, $| \downarrow\uparrow \rangle$, and $| \downarrow\downarrow \rangle$, where the first spin is of the A particle and the latter of the B particle.

For example, the part of the Hamiltonian originating from the z components is

$$J\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = J\frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{15}$$

This shows that for $H = Js_z^A \otimes s_z^B$ there are two energy levels, one with aligned spins (H_{11} for $|\uparrow\uparrow\rangle$ state and H_{44} for $|\downarrow\downarrow\rangle$ state). In this case the energy is $E = \frac{\hbar^2}{4}J$. For the usual ferromagnetic ordering, $J < 0$ and this will be the (degenerate) ground state. The states with anti-parallel spins will be higher in energy. Anti-ferromagnetic order can be observed as well in some materials and then $J > 0$ and the anti-parallel states have lower energy than the states with parallel spins.

The parts of the Hamiltonian corresponding to the x and y components can be calculated analogously to the z component, for x we obtain

$$J\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = J\frac{\hbar^2}{4}\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \tag{16}$$

and for y

$$J\frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \otimes \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = J\frac{\hbar^2}{4}\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \tag{17}$$

Overall, summing these three parts, we obtain the Hamiltonain

$$H = J\frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{18}$$

We see that the Hamiltonian is not diagonal in the direct product basis, specifically, the states with anti-parallel spins are not eigenvectors of the new Hamiltonian. In contrast, the states with aligned spins are still eigenvectors. To find the new states with anti-parallel

spins we need to diagonalise the part of the Hamiltonian corresponding to these two states

$$H_{\text{anti}} = J\frac{\hbar^2}{4}\begin{pmatrix} -1 & 2 \\ 2 & -1 \end{pmatrix}. \tag{19}$$

For the eigenvalues we readily obtain $\epsilon_{1,2} = -1\pm2$ corresponding to vectors $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. The energies of these two states are $\frac{\hbar^2}{4}J$ for the first and $-\frac{3\hbar^2}{4}J$ for the latter. Therefore, the state with symmetric spin wavefunction has the same energy as the states with both spins up or both spins down. Together, they form the triplet states with total spin $S = 1$ and projections $S_z = 1, 0, -1$. The state with anti-symmetric spin wavefunction is the singlet state with $S = 0$ and only possible projection $S_z = 0$. This can be verified by explicitly applying the operator of the magnitude of the total spin S^2 (TODO) .

G. Coupling of momenta

A spin $\hbar/2$ particle is bound in a spherically symmetric potential and is in a state with orbital momentum $l = 1\hbar$. What are the possible values of the total momentum and the projections onto the z axis?

The particle is in a state with $j = \frac{3\hbar}{2}$ and $j = \frac{\hbar}{2}$ that can be written in the product basis as

$$|\psi\rangle = |j = 3/2, j_z = 1/2, l, s\rangle = \sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle.$$

- What are the respective results when the operators j^2 and j_z act on the state $|\psi\rangle$?

- Verify, that the state $|\psi\rangle$ is also an eigenstate of the operator $j_z = l_z \otimes 1 + 1 \otimes s_z$ in the product basis of the original states.

- Rewrite the operator of the magnitude of the total momentum $j^2 = (\vec{l}\otimes1+1\otimes\vec{s})^2$ using the operators $l^2, l_z, l_-, l_+, s^2, s_z, s_-, s_+$ and verify that the state $|\psi\rangle$ is an eigenstate of j^2.

Solution:

The rules for combining angular momenta give two possible values for the total momentum: $j = \frac{3\hbar}{2}$ and $j = \frac{\hbar}{2}$. The possible projections are $j_z = \frac{3\hbar}{2}, \frac{\hbar}{2}, -\frac{\hbar}{2}$, and $-\frac{3\hbar}{2}$ for the first and $j_z = \frac{\hbar}{2}$ and $-\frac{\hbar}{2}$ for the latter.

The state $|\psi\rangle$ corresponds to $j = \frac{3\hbar}{2}$ and $j_z = \frac{\hbar}{2}$, after acting with j^2 we obtain

$$j^2|j = 3/2, j_z = 1/2, l, s\rangle = \frac{3}{2}(\frac{3}{2}+1)\hbar^2|j = 3/2, j_z = 1/2, l, s\rangle = \frac{15}{4}\hbar^2|j = 3/2, j_z = 1/2, l, s\rangle.$$

For the projection onto the z axis we obtain

$$j_z|j = 3/2, j_z = 1/2, l, s\rangle = \frac{\hbar}{2}|j = 3/2, j_z = 1/2, l, s\rangle.$$

We will now use the product basis where operators of the individual momenta act. For the projection onto the z axis we obtain

$$(l_z \otimes 1 + 1 \otimes s_z)[\sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle]$$

$$= \sqrt{\frac{2}{3}}(l_z \otimes 1)|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}(s_z \otimes 1)|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle$$

$$+ \sqrt{\frac{1}{3}}(l_z \otimes 1)|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}(s_z \otimes 1)|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle$$

$$= \sqrt{\frac{2}{3}}0\hbar|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}\frac{\hbar}{2}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle$$

$$+ \sqrt{\frac{1}{3}}\hbar|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle - \sqrt{\frac{1}{3}}\frac{\hbar}{2}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle$$

$$= \frac{\hbar}{2}\sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \frac{\hbar}{2}\sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle$$

$$= \frac{\hbar}{2}|\psi\rangle.$$

That is, the results obatained in the product and coupled basis are identical, as they should.

The operator of the magnitude of the total momentum j^2 can be expressed as

$$j^2 = (l \otimes 1 + 1 \otimes s)^2 = (l^2 \otimes 1 + 1 \otimes s^2 + 2l_x \otimes s_x + 2l_y \otimes s_y + 2l_z \otimes s_z).$$

Using $l_x = \frac{1}{2}(l_+ + l_-)$ a $l_x = \frac{1}{2i}(l_+ - l_-)$ and similarly for the spin component, we rewrite the x and y components as

$$l_x \otimes s_x + l_y \otimes s_y =$$

$$= \frac{1}{4}(l_+ + l_-) \otimes (s_+ + s_-) - \frac{1}{4}(l_+ - l_-) \otimes (s_+ - s_-)$$

$$= \frac{1}{2}(l_- \otimes s_+ + l_+ \otimes s_-).$$

Overall, we have

$$j^2 = (l^2 \otimes 1 + 1 \otimes s^2 + l_- \otimes s_+ + l_+ \otimes s_- + 2l_z \otimes s_z).$$

The state $|\psi\rangle$ is an eigenstate of both l^2 and s^2, with eigenvalues $2\hbar^2$ and $\frac{3\hbar^2}{4}$, respectively. The remaining contributions can be found by explicitly applying the operators on the states. For the first remaining term

$$l_- \otimes s_+ [\sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle],$$

the action on the first component will give zero, $s_+|s, s_z = +\frac{1}{2}\rangle = 0$, as the spin projection onto the z axis is already maximal. We then have to evaluate

$$l_- \otimes s_+ \sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle$$

$$= \hbar^2 \sqrt{\frac{1}{3}}\sqrt{1(1+1) - 1(1-1)}\sqrt{\frac{1}{2}(\frac{1}{2}+1) - (-\frac{1}{2})(-\frac{1}{2}+1)}|l, l_z = 0; s, s_z = \frac{1}{2}\rangle$$

$$= \hbar^2 \sqrt{\frac{1}{3}}\sqrt{2}\sqrt{1}|l, l_z = 0; s, s_z = \frac{1}{2}\rangle$$

$$= \hbar^2 \sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = \frac{1}{2}\rangle$$

In the term

$$l_+ \otimes s_- [\sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle],$$

the second contribution will be zero as the l projection is the largest and the spin projection is the lowest possible. We therefore need to evaluate

$$l_+ \otimes s_- \sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = \frac{1}{2}\rangle$$

$$= \hbar^2 \sqrt{\frac{2}{3}}\sqrt{1(1+1) - 0(0+1)}\sqrt{\frac{1}{2}(\frac{1}{2}+1) - (\frac{1}{2})(\frac{1}{2}-1)}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle$$

$$= \hbar^2 \sqrt{\frac{2}{3}}\sqrt{2}\sqrt{1}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle$$

$$= \hbar^2 \frac{2}{\sqrt{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle.$$

Finally, the term containing the projections onto the z axis becomes

$$2l_z \otimes s_z [\sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle]$$

$$= 2(0\hbar)(\frac{\hbar}{2})\sqrt{\frac{2}{3}}|l, l_z = 0; s, s_z = +\frac{1}{2}\rangle + 2(\hbar)(-\frac{\hbar}{2})\sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle$$

$$= -\hbar^2 \sqrt{\frac{1}{3}}|l, l_z = 1; s, s_z = -\frac{1}{2}\rangle.$$

Summing the last three results we find

$$(l_- \otimes s_+ + l_+ \otimes s_- + 2l_z \otimes s_z)|\psi\rangle =$$

$$=\hbar^2\sqrt{\frac{2}{3}}|l,l_z=0;s,s_z=\frac{1}{2}\rangle + \hbar^2\frac{2}{\sqrt{3}}|l,l_z=1;s,s_z=-\frac{1}{2}\rangle$$

$$- \hbar^2\sqrt{\frac{1}{3}}|l,l_z=1;s,s_z=-\frac{1}{2}\rangle$$

$$=\hbar^2\sqrt{\frac{2}{3}}|l,l_z=0;s,s_z=\frac{1}{2}\rangle + \hbar^2\sqrt{\frac{1}{3}}|l,l_z=1;s,s_z=-\frac{1}{2}\rangle$$

$$=\hbar^2[\sqrt{\frac{2}{3}}|l,l_z=0;s,s_z=\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|l,l_z=1;s,s_z=-\frac{1}{2}\rangle]$$

$$=\hbar^2|\psi\rangle\,.$$

Therefore, $|\psi\rangle$ is an eigenstate of the operator $2l \cdot s$ with an eigenvalue of $\hbar^2$. Together with the contributions of l^2 and s^2 the total eigenvalue of j^2 is $(2 + \frac{3}{4} + 1)\hbar^2 = \frac{15}{4}\hbar^2$, as it should for $j = \frac{3}{2}\hbar$.