Física Quântica I / Mecânica Quântica (2021/22)

Folha de Problemas 11 (Potenciais em 3D. Momento angular.)

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— Soluções —

Problema 1 | Potencial separável em coordenadas Cartesianas

Uma partícula de massa M é confinada pelo seguinte potencial tridimensional:

$$\mathcal{V}(x,y,z) = \mathcal{U}(x,y) + \mathcal{W}(z),$$

sendo

$$\mathcal{U}(x,y) = \frac{1}{2}M\omega^2\left(x^2+y^2\right), \qquad \mathcal{W}(z) = \begin{cases} 0, & 0 \le z \le a \\ +\infty, & \text{restantes } z \end{cases}.$$

Este potencial $\mathcal{V}(x,y,z)$ é quadrático no plano $\mathcal{O}xy$ e consiste num poço infinito segundo a direção z. Como $\mathcal{V} \xrightarrow[r\to\infty]{} +\infty$, o potencial é confinante para qualquer energia e segundo qualquer direção; portanto, tem apenas autoestados ligados e o espectro de energia é discreto.

1. Determine o espectro de energia desta partícula, mostrando que ele é caraterizado por três números quânticos m, n, l,

   $$E_{m,n,l} = \ldots ? \ldots$$

   Indique que valores pode tomar cada um dos números quânticos m, n, l e determine a energia do estado fundamental.

2. Escreva a função $\varphi_{\text{gs}}(x,y,z)$ que representa a função de onda normalizada do estado fundamental.

3. A simetria deste potencial no plano $\mathcal{O}xy$ leva a que o espectro de energia seja degenerado. Determine a degenerescência/multiplicidade do nível $E_{m,n,l}$ como função de m, n, l.

Nota: Repare que o Hamiltoniano desta partícula pode ser expresso na forma separável $\hat{H} = \hat{H}^{(x)} + \hat{H}^{(y)} + \hat{H}^{(z)}$ discutida na Lição 20. Não recalcule nada que já seja um resultado conhecido de aulas ou de folhas de problemas anteriores; siga o procedimento descrito na Lição 20 para abordar este tipo de Hamiltoniano.

Solution

1. The Hamiltonian for this problem is

$$\begin{aligned}\hat{H} &= \frac{\hat{\mathrm{P}}^2}{2M} + \mathcal{V}(\hat{\mathrm{R}}) \\ &= \frac{\hat{\mathrm{P}}_x^2}{2M} + \frac{\hat{\mathrm{P}}_y^2}{2M} + \frac{\hat{\mathrm{P}}_z^2}{2M} + \frac{1}{2}M\omega^2\left(\hat{\mathrm{X}}^2 + \hat{\mathrm{Y}}^2\right) + \mathcal{W}(\hat{Z}) \\ &= \left[\frac{\hat{\mathrm{P}}_x^2}{2M} + \frac{1}{2}M\omega^2\hat{\mathrm{X}}^2\right] + \left[\frac{\hat{\mathrm{P}}_y^2}{2M} + \frac{1}{2}M\omega^2\hat{\mathrm{Y}}^2\right] + \left[\frac{\hat{\mathrm{P}}_z^2}{2M} + +\mathcal{W}(\hat{Z})\right] \\ &= \hat{H}^{(1)} + \hat{H}^{(2)} + \hat{H}^{(3)}\end{aligned}$$

where

$$\hat{H}^{(1)} \equiv \frac{\hat{\mathrm{P}}_x^2}{2M} + \frac{1}{2}M\omega^2\hat{\mathrm{X}}^2, \qquad \hat{H}^{(2)} \equiv \frac{\hat{\mathrm{P}}_y^2}{2M} + \frac{1}{2}M\omega^2\hat{\mathrm{Y}}^2, \qquad \hat{H}^{(3)} \equiv \frac{\hat{\mathrm{P}}_z^2}{2M} + +\mathcal{W}(\hat{Z}).$$

We see that:

(i) the total Hamiltonian is the sum of 3 independent Hamiltonians, each defined in an independent state space (Hilber space);

(ii) $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ are just two "copies" of the 1D harmonic oscillator Hamiltonian;

(iii) $\hat{H}^{(3)}$ is the Hamiltonian for an infinite potential well of size a in the z direction.

Therefore, the energy eigenvalues are given by

$$E = E^{(1)} + E^{(2)} + E^{(3)},$$

where $E^{(i)}$ represents the eigenvalues of the one-dimensional problem defined by the Hamiltonian $\hat{H}^{(i)}$ for the motion along the direction $i \in \{x, y, z\}$. The energy eigenfunctions are

$$\varphi(x, y, z) = \varphi^{(1)}(x)\,\varphi^{(2)}(y)\,\varphi^{(3)}(z),$$

where each $\varphi^{(i)}$ is an eigenfunction of the 1D problem for the motion along the direction i. In other words,

$$\hat{H}^{(1)}\varphi^{(1)}(x) = E^{(1)}\varphi^{(1)}(x), \qquad \hat{H}^{(2)}\varphi^{(2)}(y) = E^{(2)}\varphi^{(2)}(y), \qquad \hat{H}^{(3)}\varphi^{(3)}(z) = E^{(3)}\varphi^{(3)}(z).$$

Since $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ are Hamiltonians for an harmonic potential, their corresponding eigenvalues are

$$E^{(1)} = E^{(1)}_m = \hbar\omega\left(m + \frac{1}{2}\right), \qquad E^{(2)} = E^{(2)}_n = \hbar\omega\left(n + \frac{1}{2}\right), \qquad m, n = 0, 1, 2, \ldots$$

and, according to our discussion in the lectures about the 1D harmonic oscillator (see notes for Lesson 19), the corresponding normalized eigenstates will be

$$\begin{aligned}\varphi^{(1)}_m(x) &= \sqrt{\frac{\alpha_0}{2^n\sqrt{\pi}\,n!}}e^{-\frac{1}{2}\alpha_0^2x^2}H_m\Big(\alpha_0 x\Big), \\ \varphi^{(2)}_n(y) &= \sqrt{\frac{\alpha_0}{2^n\sqrt{\pi}\,n!}}e^{-\frac{1}{2}\alpha_0^2y^2}H_m\Big(\alpha_0 y\Big),\end{aligned}$$

where $\alpha_0 = \sqrt{\frac{M\omega}{\hbar}}$ and $H_m(x)$ is the m-order Hermite polynomial.

The Hamiltonian $\hat{H}^{(3)}$ is a 1D infinite potential well defined in the region $0 \leq z \leq a$. The corresponding spectrum and eigenfunctions are

$$E^{(3)} = E_l^{(3)} = \frac{\hbar^2\pi^2}{2Ma^2}\, l^2, \qquad \varphi_l^{(3)}(z) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{l\pi z}{a}\right), \qquad l = 1, 2, 3, \ldots$$

Combining all these results, we conclude that energy eigenvalues of this particle in the 3D potential $\mathcal{V}(\boldsymbol{r})$ are given by

$$E_{m,n,l} = E_m^{(1)} + E_n^{(2)} + E_l^{(3)} = \hbar\omega\,(m+n+1) + \frac{\hbar^2\pi^2}{2Ma^2}\, l^2,$$

where $m, n = 0, 1, 2, \ldots$ and $l = 1, 2, 3, \ldots$. The ground state energy (E_{gs}) should be the minimum possible value of $E_{m,n,l}$ which is obtained when $m = n = 0$ and $l = 1$:

$$E_{\text{gs}} = E_{0,0,1} = \hbar\omega + \frac{\hbar^2\pi^2}{2Ma^2}.$$

2. As written in the response to the previous question, the normalized eigenfunction in this problem is given by

$$\varphi_{mnl}(x, y, z) = \varphi_m^{(1)}(x)\,\varphi_n^{(2)}(y)\,\varphi_l^{(3)}(z),$$

where the $\varphi^{(i)}$ are the normalized wavefunctions of the three independent Hamiltonians. We saw above that the ground state energy corresponds to $(m, n, l) = (0, 0, 1)$ and, therefore, the associated eigenfunction is

$$\varphi_{001}(x, y, z) = \varphi_0^{(1)}(x)\,\varphi_0^{(2)}(y)\,\varphi_1^{(3)}(z) = \sqrt{\frac{2\alpha_0^2}{\pi a}}\, e^{-\frac{1}{2}\alpha_0^2(x^2+y^2)}\,\sin\left(\frac{l\pi z}{a}\right).$$

Since we used each of the individual $\varphi_0^{(1)}(x)$, $\varphi_0^{(2)}(y)$, $\varphi_0^{(3)}(z)$ already normalized, the result is guaranteed to be normalized in the entire space (you can verify it explicitly by computing $\int dx \int dy \int dz\ |\varphi_{001}(x, y, z)|^2$).

3. From the expression obtained above for the energy eigenvalues

$$E_{m,n,l} = \hbar\omega\,(m+n+1) + \frac{\hbar^2\pi^2}{2Ma^2}\, l^2, \tag{1.1}$$

it is obvious that any combination of integers m and n such that $m + n = \lambda$ will correspond to the same energy. The question is then, how many ways are there of combining two non-negative integers, so that their sum is λ? For each λ we can choose $m \in \{0, 1, \ldots, \lambda\}$ and, once we choose m, the value of n is constrained by the condition $\lambda = m + n$. Therefore, we have $\lambda + 1$ ways to write the integer λ as the sum of two other non-negative integers. The degeneracy $g(m, n, l)$ of an energy level E_{mnl} is therefore

$$g(m, n, l) = m + n + 1. \tag{1.2}$$

As an explicit example it is clear from the expression for the energy eigenvalues given in equation (1.1) that, irrespective of the value of l,

$$E_{2,3,l} = E_{3,2,l} = E_{1,4,l} = E_{4,1,l} = E_{0,5,l} = E_{5,0,l} = 6\hbar\omega + \frac{\hbar^2\pi^2}{2Ma^2}\, l^2.$$

This means there are 6 different states all with the same energy (that's why we call them degenerate), in agreement with equation (1.2), which says the degeneracy of this value of energy should be

$$g(2,3,l) = 6.$$

Note that the last term in (1.1) proportional to l^2 does not enter in the consideration of the degeneracy. That is because any additional degeneracy arising from it would be purely accidental and dependent on a particular combination of the parameters ω and a that characterize the potential. In contrast, we have complete freedom in interchanging m and n because of the symmetry of the potential in the xy plane, irrespective of what values ω, a may take.

Problema 2 | Espectro e autoestados de momento angular

Os valores próprios e autoestados dos operadores $\hat{L}^2$ e $\hat{L}_z$ de momento angular orbital são definidos pelas relações

$$\hat{L}^2|l,m\rangle = l(l+1)\hbar^2\,|l,m\rangle, \qquad \hat{L}_z|l,m\rangle = m\hbar\,|l,m\rangle.$$

Os operadores de escada $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$ permitem relacionar estes autoestados normalizados através de

$$|l,m+1\rangle = \frac{\hat{L}_+}{\hbar\gamma_+}|l,m\rangle, \qquad |l,m-1\rangle = \frac{\hat{L}_-}{\hbar\gamma_-}|l,m\rangle.$$

1. Determine as constantes positivas $\gamma_\pm$ que garantem que $|l,m\pm1\rangle$ estará normalizado quando $|l,m\rangle$ também o for.

2. Os harmónicos esféricos $Y_l^m(\theta,\phi) \equiv \langle \boldsymbol{r}|l,m\rangle$ são as funções que definem a dependência angular dos autoestados $|l,m\rangle$. Sabendo que

$$Y_2^0(\theta,\phi) = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right),$$

obtenha o harmónico esférico $Y_2^1(\theta,\phi) = \langle \boldsymbol{r}|2,1\rangle$ usando as relações referidas na questão anterior.

3. Se uma partícula estiver no autoestado de momento angular $|l,m\rangle = |2,1\rangle$, qual é a probabilidade de a encontrar na região $x \geq 0 \wedge y \geq 0 \wedge z \geq 0$ (o primeiro octante)?

4. Calcule o valor esperado de $\hat{L}_x^2$ no estado $|1,1\rangle$ recorrendo aos dois métodos seguintes:

   a) exprimindo este operador em termos de $\hat{L}_\pm$ e recorrendo às relações algébricas entre autoestados $|l,m\rangle$;

   b) avaliando diretamente o integral correspondente,

$$\langle 1,1|\hat{L}_x^2|1,1\rangle = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi\,\left[Y_1^1(\theta,\phi)\right]^*\,\hat{L}_x^2\,Y_1^1(\theta,\phi),$$

   tendo em conta que $Y_1^{\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\,\sin\theta\,e^{\pm i\phi}$.

Nota: Em coordenadas esféricas,

$$\hat{L}_x = i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right], \quad \hat{L}_y = i\hbar\left[-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right], \quad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}.$$

Solution

1. Taking the inner product of each side of the equation

$$|l, m \pm 1\rangle = \frac{\hat{L}_\pm}{\hbar\gamma_\pm}|l, m\rangle$$

with itself leads to

$$\hbar^2|\gamma_\pm|^2\,\langle l, m \pm 1|l, m \pm 1\rangle = \langle l, m|\hat{L}_\mp\hat{L}_\pm|l, m\rangle.$$

Now note that

$$\begin{aligned}\hat{L}_\mp\hat{L}_\pm &= \big(\hat{L}_x \mp i\hat{L}_y\big)\big(\hat{L}_x \pm i\hat{L}_y\big)\\ &= \hat{L}_x^2 + \hat{L}_y^2 \pm i\left(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x\right)\\ &= \hat{L}^2 - \hat{L}_z^2 \mp \hbar L_z.\end{aligned}$$

In order to be normalized, we should have $\langle l, m \pm 1|l, m \pm 1\rangle = 1$ which implies

$$|\gamma_\pm|^2 = \hbar^{-2}\langle l, m|\hat{L}_\mp\hat{L}_\pm|l, m\rangle = \hbar^{-2}\langle l, m|\hat{L}^2 - \hat{L}_z^2 \mp \hbar L_z|l, m\rangle = l(l+1) - m^2 \mp m.$$

Therefore, choosing the positive root, we obtain

$$\gamma_\pm = \sqrt{l(l+1) - m(m \pm 1)}.$$

2. We can obtain the target eigenstate from the one given using the relation provided in question 1:

$$|l, m+1\rangle = \frac{\hat{L}_+}{\hbar\gamma_+}|l, m\rangle = \frac{\hat{L}_+}{\hbar\sqrt{l(l+1) - m(m+1)}}|l, m\rangle$$

by applying it to the case $l = 2$, $m = 0$:

$$|2, 1\rangle = \frac{1}{\hbar\sqrt{6}}\hat{L}_+|2, 0\rangle \qquad \xrightarrow{\text{spherical representation}} \qquad Y_2^1 = \frac{1}{\hbar\sqrt{6}}\hat{L}_+Y_2^0,$$

where the spherical representation of $\hat{L}_+$ is obtained directly from the expressions provided in the text of the problem for $\hat{L}_x$ and $\hat{L}_y$. So,

$$\hat{L}_+ = i\hbar\left[\big(\sin\phi - i\cos\phi\big)\frac{\partial}{\partial\theta} + \big(\cos\phi + i\sin\phi\big)\cot\theta\,\frac{\partial}{\partial\phi}\right] = \hbar e^{i\phi}\left[\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right].$$

Hence,

$$\begin{aligned}Y_2^1(\theta,\phi) &= \frac{1}{\hbar\sqrt{6}}\hat{L}_+Y_2^0 = \frac{1}{\hbar\sqrt{6}}\hat{L}_+\left[\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)\right]\\ &= \sqrt{\frac{5}{96\pi}}\,e^{i\phi}\left[\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right]\left(3\cos^2\theta - 1\right)\\ &= \sqrt{\frac{45}{96\pi}}\,e^{i\phi}\frac{\partial}{\partial\theta}\big(\cos^2\theta\big) = -\sqrt{\frac{15}{8\pi}}\,\sin\theta\cos\theta e^{i\phi}.\end{aligned}$$

3. The first octant corresponds to the angular ranges

$$0 \le \theta \le \frac{\pi}{2}, \qquad 0 \le \phi \le \frac{\pi}{2},$$

and, therefore, such probability is given by

$$\mathcal{P} = \int_0^{\frac{\pi}{2}} d\phi \int_0^{\frac{\pi}{2}} d\theta \sin\theta \left|Y_2^1(\theta,\phi)\right|^2 = \frac{15}{8\pi} \int_0^{\frac{\pi}{2}} d\phi \int_0^{\frac{\pi}{2}} d\theta\, \sin^3\theta \cos^2\theta$$

$$\Big\downarrow \text{ change variable } (u \equiv \cos\theta)$$

$$= \frac{15}{16} \int_0^1 du\, u^2(1-u^2) = \frac{1}{8}.$$

4.

a) The first method is quick and clean:

$$\langle 1,1|\hat{L}_x^2|1,1\rangle = \langle 1,1|\left(\frac{\hat{L}_+ + \hat{L}_-}{2}\right)^2 |1,1\rangle = \frac{1}{4}\langle 1,1|\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+|1,1\rangle$$
$$= \frac{1}{2}\left[l(l+1) - m^2\right]\Big|_{l=1,m=1} = \frac{\hbar^2}{2}.$$

b) This second approach will take more time. The first thing to do is to apply the operator

$$\hat{L}_x = i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]$$

twice to the function $Y_1^1(\theta,\phi)$. The operator $\hat{L}_x^2$ in spherical coordinates becomes

$$\hat{L}_x^2 = -\hbar^2\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]$$

$$-\hbar^{-2}\hat{L}_x^2 = \sin^2\phi\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\cos\phi\frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$+ \sin\phi\cos\phi\frac{\partial}{\partial\phi}\frac{\partial}{\partial\theta}\cot\theta + \cot\theta\cos\phi\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi}\sin\phi$$

Now apply each term to $Y_1^1(\theta,\phi)$:

$$\frac{\partial^2}{\partial\theta^2}\left[\sin\theta e^{i\phi}\right] = -\sin\theta e^{i\phi}$$
$$\frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial}{\partial\phi}\right)\left[\sin\theta e^{i\phi}\right] = -e^{2i\phi}\sin\theta$$
$$\frac{\partial}{\partial\phi}\frac{\partial}{\partial\theta}\left[\cot\theta\sin\theta e^{i\phi}\right] = -i\sin\theta e^{i\phi}$$
$$\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi}\left[\sin\phi\sin\theta e^{i\phi}\right] = \cos\theta e^{2i\phi}$$

Put everything together,

$$\left[Y_1^1(\theta,\phi)\right]^* \hat{L}_x^2\, Y_1^1(\theta,\phi) = -\frac{3\hbar^2}{8\pi}\left[-\sin^2\theta\sin^2\phi - i\sin^2\theta\sin\phi\cos\phi\right]$$
$$= -\frac{3\hbar^2}{8\pi}\left[i\sin^2\theta\sin\phi e^{i\phi}\right]$$

and integrate to obtain the expectation value of $\hat{L}_x^2$:

$$\begin{aligned}
\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left[Y_1^1(\theta,\phi)\right]^* \hat{L}_x^2\, Y_1^1(\theta,\phi) &= -\frac{3i\hbar^2}{8\pi}\int_0^\pi \sin^3\theta d\theta \int_0^{2\pi} d\phi \sin\phi e^{i\phi} \\
&= \frac{3\hbar^2}{8}\int_0^\pi \sin^3\theta d\theta \\
&= \frac{3\hbar^2}{8}\int_{-1}^1 \sin^2\theta\, d(\cos\theta) \\
&= \frac{\hbar^2}{2}.
\end{aligned}$$

The final result is thus

$$\langle 1,1|\hat{L}_x^2|1,1\rangle \equiv \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left[Y_1^1(\theta,\phi)\right]^* \hat{L}_x^2\, Y_1^1(\theta,\phi) = \frac{\hbar^2}{2},$$

which, as expected, is precisely the same obtained before in a much more expedite way using the algebra of the raising and lowering operators.

■

Problema 3 | Poços de potencial isotrópicos em 3D

Vimos anteriormente que, em uma dimensão, um poço de potencial *simétrico* admite, pelo menos, um estado ligado. A situação é diferente em 2 e 3 dimensões, como veremos nos dois exemplos seguintes de potenciais tridimensionais para uma partícula de massa m.

Para cada um dos potenciais abaixo, que dependem apenas da distância radial à origem (r), *mostre* que só existem estados ligados se $\Omega > \Omega_c$ e *determine* o valor crítico Ω_c. Considere apenas soluções com momento angular $l = 0$ (*porque o estado fundamental tem* $l = 0$).

1. Partícula confinada num poço de potencial esférico:

$$V(\boldsymbol{r}) = \begin{cases} -\Omega, & 0 \le r \le a \\ 0, & r > a \end{cases}, \qquad (\Omega > 0).$$

2. Partícula confinada por uma barreira esférica do tipo delta de Dirac:

$$V(\boldsymbol{r}) = -\frac{\hbar^2\Omega}{2m}\,\delta(r-a), \qquad (\Omega > 0).$$

Solution

Since both potentials are isotropic and depend only on the distance r to the origin, the energy eigenstates will have the general form

$$\varphi_{n,l,m}(\boldsymbol{r}) = R_{n,l}(r) Y_l^m(\theta,\phi),$$

where $Y_l^m(\theta,\phi)$ are the spherical harmonics. Hence, whether an energy eigenstate is bound or not is determined by the behaviour of the radial portion of the wavefunction (whether it is decaying with r). We should then concentrate on the radial equation, which is

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right] R_{n,l}(r) = E_{n,l}\, R_{n,l}(r)$$

or

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right] u_{n,l}(r) = E_{n,l}\, u_{n,l}(r)$$

where we performed the usual substitution

$$u_{n,l}(r) \equiv r\, R_{n,l}(r).$$

Since the repulsive part in the effective potential

$$V_{\text{eff}}(r) \equiv \frac{l(l+1)\hbar^2}{2mr^2} + V(r)$$

increases with l, the ground state will have $l = 0$ (because this corresponds to the case where V_{eff} is the deepest, most attractive). When $l = 0$, the radial equation simplifies to

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r)\right] u_{n,0}(r) = E_{n,0}\, u_{n,0}(r),$$

which is exactly the same equation we would have in a one-dimensional potential problem, except for a very important difference: the solution $u(r)$ must satisfy the boundary condition at the origin

$$u_{n,l}(0) = 0.$$

1. Bound solutions of this potential will correspond to the solutions that decay in the region $r > a$. We re-write the radial equation for $u(r)$ as

$$u''(r) = -\frac{2mE}{\hbar^2}\left[E - V(r)\right] u(r) = \begin{cases} -\frac{2m}{\hbar^2}\left[E + \Omega\right] u(r), & 0 \le r \le a \\ \\ -\frac{2m}{\hbar^2} E\, u(r), & r > a \end{cases}.$$

From here, we see that decaying (bound) solutions will only be possible if $E < 0$. Introducing

$$k \equiv \sqrt{\frac{2m(\Omega - |E|)}{\hbar^2}}, \qquad \lambda \equiv \sqrt{\frac{2m|E|}{\hbar^2}}, \qquad E = -|E|,$$

the general solution will be

$$u(r) = \begin{cases} A\cos(kr) + B\sin(kr), & 0 \le r \le a \\ Ce^{-\lambda r}, & r > a \end{cases}.$$

This solution must fulfil the boundary condition at the origin and be continuous at $r = a$:

$$u(0) = 0, \qquad u(a^+) = u(a^-), \qquad u'(a^+) = u'(a^-),$$

which translates into

$$A = 0, \qquad B\sin(ka) = Ce^{-\lambda a}, \qquad Bk\cos(ka) = -\lambda Ce^{-\lambda a}.$$

Dividing the last two we obtain

$$ka\,\cot(ka) = -\sqrt{\frac{2m\Omega a^2}{\hbar^2} - (ka)^2}.$$

This is a transcendental equation whose roots determine the bound solutions. At this point, you should draw a sketch of both sides of this equation as a function of ka in order to analyse graphically the conditions for the existence of solutions. From the graph, you should see that, since $k > 0$, there sill be solutions only if $ka > \pi/2$; this is because, for smaller ka, the cotangent never takes negative values and the right-hand side of this equation is negative. The argument of the square root must also be positive for a solution to exist. These two conditions are thus

$$ka > \frac{\pi}{2} \qquad \text{and} \qquad \frac{2m\Omega a^2}{\hbar^2} - (ka)^2 > 0.$$

The smallest Ω that fulfils these two conditions is therefore (the graphical sketch helps to visualise this)

$$\frac{2m\Omega a^2}{\hbar^2} - \frac{\pi^2}{4} > 0 \qquad \Rightarrow \qquad \Omega_c = \frac{\hbar^2\pi^2}{8ma^2}.$$

In conclusion, only if $\Omega > \Omega_c$ do we have bound solutions for a particle in this potential.

2. This potential is zero everywhere, except exactly at $r = a$, where we have an attractive Dirac-delta potential. Therefore, any bound solution must have $E < 0$. The general solution of the radial equation for negative energies is therefore (write $E = -|E|$)

$$u''(r) = \frac{2m}{\hbar^2}|E|\,u(r) \qquad \Rightarrow \qquad u(r) = \begin{cases} A\sinh(\lambda r) + B\cosh(\lambda r), & r \le a \\ Ce^{-\lambda r} & r \ge a \end{cases}$$

where

$$\lambda \equiv \sqrt{\frac{2m|E|}{\hbar^2}}.$$

The Dirac-delta introduces a discontinuity in the derivative at $r = a$, and thus the boundary conditions to fulfil are

$$u(0) = 0, \qquad u(a^+) = u(a^-), \qquad u'(a^+) - u'(a^-) = -\Omega\,u(a).$$

These imply, respectively,

$$B = 0, \qquad A\sinh(\lambda a) = Ce^{-\lambda a}, \qquad -\lambda Ce^{-\lambda a} - \lambda A\cosh(\lambda a) = -\Omega Ce^{-\lambda a}.$$

Solving for the last two we obtain

$$1 - e^{-2\lambda a} = \frac{2\lambda a}{\Omega a} \qquad \Leftrightarrow \qquad 1 - e^{-\xi} = \frac{\xi}{\Omega a}, \quad \xi \equiv 2\lambda a.$$

This is a transcendental equation whose roots determine the bound solutions for this potential. As in the previous question, you should graphically sketch the dependence of both sides on the parameter ξ, in order to graphically inspect the conditions for the existence of solution(s).

As a function of the parameter $\xi \equiv 2\lambda a$, the left-hand side of the above equation grows monotonically from 0 to 1, while the right-hand side is linear in ξ. There will be precisely one solution if the slope at the origin of the curve representing the left-hand side is *greater* than the slope of the right-hand side (it is the only situation in which the curves representing the two sides of the equation intersect). The slope at the origin of the left-hand side is

$$\text{slope L.H.S.} = \frac{d}{d\xi}(1 - e^{-\xi})\Big|_{\xi=0} = 1,$$

while

$$\text{slope R.H.S.} = \frac{d}{d\xi}\Big(\frac{\xi}{\Omega a}\Big)\Big|_{\xi=0} = \frac{1}{\Omega a}.$$

So, the condition for the solution is

$$1 > \frac{1}{\Omega a} \qquad \Rightarrow \qquad \Omega > \frac{1}{a} \qquad \longrightarrow \qquad \Omega_c = \frac{1}{a}.$$

This is the minimum value of Ω required for a solution to exist. As the graphical sketch will show, there is only one solution in this case.

Problema 4 | Átomo de hidrogénio

Designa-se por ião hidrogenoide um ião com apenas um eletrão. Do ponto de vista do eletrão, a situação é equivalente à do átomo de hidrogénio, mas com uma carga elétrica maior no núcleo. Supondo que essa carga nuclear é $+Ze$, o Hamiltoniano do eletrão no potencial de Coulomb criado pelo núcleo é o seguinte:

$$\hat{H} = \frac{\hat{\boldsymbol{P}}^2}{2m} - \frac{Zq^2}{r}, \qquad q^2 \equiv \frac{e^2}{4\pi\varepsilon_0}.$$

O estado *fundamental* desse eletrão é caraterizado pela função de onda

$$\varphi_{\text{gs}}(\boldsymbol{r}) = R(r)Y_0^0(\theta,\phi), \qquad Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}},$$

que tem apenas dependência radial com a seguinte forma:

$$R(r) = \mathcal{N}\, e^{-\lambda r}, \qquad \lambda > 0.$$

1. Determine a constante de normalização $\mathcal{N}$ da função $R(r)$.

2. Mostre que a constante λ e a energia do estado fundamental do eletrão são dadas, respetivamente, por

$$\lambda = \frac{Z}{a_0}, \qquad \text{e} \qquad E_{\text{gs}} = -Z^2 R_H,$$

   onde $R_H \equiv \frac{q^4 m}{2\hbar^2}$ é a constante de Rydberg e $a_0 \equiv \frac{\hbar^2}{mq^2}$ é o raio de Bohr. *Sugestão: use o facto de que $R(r)$ é solução da equação radial.*

3. Calcule o valor esperado da energia potencial deste eletrão no estado fundamental.

4. Mostre que, no estado fundamental, os valores esperados da energia cinética e potencial são
$$\langle\hat{T}\rangle = -\frac{1}{2}\langle\hat{V}\rangle = -E_{\text{gs}}.$$

5. Determine $\langle r\rangle$ e o raio mais provável do eletrão no estado fundamental.

Informação útil:
$$\int_0^\infty r^p e^{-\lambda r} dr = \frac{p!}{\lambda^{p+1}}.$$

Solution

1. The normalization condition for any 3-dimensional wavefunction, $\psi(\boldsymbol{r})$, is (all are equivalent forms)
$$1 = \int |\psi(\boldsymbol{r})|^2 d\boldsymbol{r} = \int |\psi(\boldsymbol{r})|^2\, dxdydz = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\, d\theta \int_0^\infty |\psi(\boldsymbol{r})|^2\, r^2 dr.$$
As the Coulomb potential is spherically symmetric, we use the last of the above versions:
$$\begin{aligned}1 &= \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\, d\theta \int_0^\infty |\varphi_{\text{gs}}(\boldsymbol{r})|^2\, r^2 dr = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\, d\theta \int_0^\infty \left|R(\boldsymbol{r})Y_0^0(\theta,\phi)\right|^2\, r^2 dr\\ &= \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^\pi \sin\theta\, d\theta \int_0^\infty |R(\boldsymbol{r})|^2\, r^2 dr = \int_0^\infty |R(\boldsymbol{r})|^2\, r^2 dr\\ &= \mathcal{N}^2 \int_0^\infty e^{-2\lambda r}\, r^2 dr.\end{aligned}$$
The problem text provides the following integral:
$$\int_0^\infty r^p e^{-\lambda r} dr = \frac{p!}{\lambda^{p+1}},$$
which we use in the expression above to obtain the normalization constant
$$1 = \mathcal{N}^2 \int_0^\infty e^{-2\lambda r}\, r^2 dr = \frac{2!\,\mathcal{N}^2}{(2\lambda)^3} \qquad \longrightarrow \qquad \mathcal{N} = 2\lambda^{3/2}.$$
So, the normalized wavefunction is
$$\varphi_{\text{gs}}(\boldsymbol{r}) = \frac{2\lambda^{3/2}}{\sqrt{2\pi}}\, e^{-\lambda r}.$$

2. Taking into account that the provided wavefunction has angular momentum quantum number $l = 0$, the radial equation will be
$$\left[-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}r + V(r)\right] R(r) = E\, R(r).$$
Replacing here the wavefunction provided for the ground state, $R(r) = \mathcal{N}e^{-\lambda r}$, we obtain
$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}\left(re^{-\lambda r}\right) - \frac{Zq^2}{r}e^{-\lambda r} = E_{\text{gs}}\, e^{-\lambda r} \quad\Leftrightarrow\quad -\frac{\hbar^2}{2m}\left(\lambda^2 - \frac{2\lambda}{r}\right) - \frac{Zq^2}{r} = E_{\text{gs}}.$$

This equation can be rewritten as

$$-E_{\text{gs}} - \frac{\hbar^2\lambda^2}{2m} + \left(\frac{2\lambda\hbar^2}{2m} - Zq^2\right)\frac{1}{r} = 0.$$

In order for this equation to hold for all r, the coefficients of all powers of r must vanish (including the r-independent term). In other words, we must have

$$\lambda = \frac{Zq^2 m}{\hbar^2} = \frac{Z}{a_0} \qquad \text{and} \qquad E_{\text{gs}} = -\frac{\hbar^2\lambda^2}{2m} = -\frac{Z^2q^4m}{2\hbar^2} = -\frac{Z^2q^2}{2a_0}.$$

3. The potential energy is

$$V(r) = -\frac{Zq^2}{r},$$

and its expectation value in the ground state will be

$$\begin{aligned}\langle\hat{V}\rangle &= \int \varphi_{\text{gs}}(\boldsymbol{r})^*\, V(r)\, \varphi_{\text{gs}}(\boldsymbol{r})\, d\boldsymbol{r} = \int_0^\infty r^2\,[R(r)]^2\, V(r)\, dr \\ &= \int_0^\infty r^2\,[R(r)]^2 \left(-\frac{Zq^2}{r}\right) dr = -4\lambda^3 Zq^2 \int_0^\infty r\, e^{-2\lambda}\, dr \\ &= -\frac{Z^2q^2}{a_0}.\end{aligned}$$

4. From the results of questions 2 and 3 above, we can see that

$$\langle\hat{V}\rangle = 2E_{\text{gs}}.$$

To avoid the explicit computation of the expectation value of the kinetic energy we note that, since the electronic Hamiltonian consists of the sum of kinetic and potential energies,

$$\hat{H} = \hat{T} + \hat{V} \qquad \Rightarrow \qquad \langle\hat{T}\rangle = \langle\hat{H}\rangle - \langle\hat{V}\rangle = E_{\text{gs}} - \langle\hat{V}\rangle = E_{\text{gs}} - 2E_{\text{gs}} = -E_{\text{gs}}.$$

Hence,

$$\langle\hat{T}\rangle = -E_{\text{gs}} = -\frac{\langle\hat{V}\rangle}{2}.$$

5. The expectation value is given by

$$\langle r\rangle = \int_0^\infty r|R(r)|^2\, r^2 dr = \mathcal{N}^2 \int_0^\infty r^3 e^{-2\lambda r}\, dr = \frac{\mathcal{N}^2 3!}{(2\lambda)^4} = \frac{3}{2\lambda} = \frac{3a_0}{2Z}.$$

The most likely radial position is obtained by seeking the maximum of the radial probability distribution, which is given by

$$\mathcal{P}(r) \equiv r^2|R(r)|^2.$$

To find the position of the maximum, we look for the zeros of the derivative of $\mathcal{P}(r)$:

$$\mathcal{P}(r) = \mathcal{N}^2 r^2 e^{-2\lambda r}, \qquad \frac{d\mathcal{P}(r)}{dr} = 0 \quad \Rightarrow \quad 2r - 2\lambda r^2 = 0 \quad \Rightarrow \quad r_{\text{max}} = \frac{1}{\lambda} = \frac{a_0}{Z}.$$

Problema 5 | Operadores de momento angular em coordenadas esféricas

O operador que representa o vetor momento angular orbital é definido como

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{R}} \times \hat{\boldsymbol{P}},$$

onde $\hat{\boldsymbol{R}}$ e $\hat{\boldsymbol{P}}$ são os operadores associados ao vetor posição e ao vetor momento em 3 dimensões. Recordando que na representação/base de posição temos

$$\hat{\boldsymbol{R}} \mapsto \boldsymbol{r} \quad \text{(vetor posição)}, \qquad \hat{\boldsymbol{P}} \mapsto \frac{\hbar}{i}\boldsymbol{\nabla} \quad \text{(gradiente)},$$

então o operador momento angular é representado por

$$\hat{\boldsymbol{L}} = -i\hbar\, \boldsymbol{r} \times \boldsymbol{\nabla}, \qquad (\text{"}\times\text{" significa aqui produto vetorial}).$$

1. Mostre que, em coordenadas esféricas, as projeções $\hat{L}_{x,y,z}$ são dadas por

$$\hat{L}_x = i\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right], \quad \hat{L}_y = i\hbar\left[-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right], \quad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}.$$

Nota: Para o fazer, expresse $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$, $\frac{\partial}{\partial z}$ em termos de $\frac{\partial}{\partial r}$, $\frac{\partial}{\partial \theta}$, $\frac{\partial}{\partial \phi}$, partindo das relações entre as coordenadas Cartesianas e esféricas:

$$x = r\sin\theta\,\cos\phi, \qquad y = r\sin\theta\,\sin\phi, \qquad z = r\cos\theta.$$

2. Recorrendo ao resultado anterior, obtenha a representação do operador

$$\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

em coordenadas esféricas.

3. Mostre que

$$\boldsymbol{\nabla}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{\hbar^2 r^2}\hat{\boldsymbol{L}}^2,$$

onde o *Laplaciano* em coordenadas esféricas é dado por

$$\boldsymbol{\nabla}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right].$$

Solution

1. First, let us write each component of the angular momentum explicitly:

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{R}} \times \hat{\boldsymbol{P}} \quad \longrightarrow \quad \begin{cases} \hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{cases} . \tag{5.1}$$

To convert this to spherical coordinates, we must replace

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta, \tag{$\star$}$$

and we must also convert the derivatives with respect to x, y, z into derivatives with respect to r, θ and ϕ. According to elementary differential calculus, the differentials are related by

$$\begin{aligned} dx &= \frac{\partial x}{\partial r}\,dr + \frac{\partial x}{\partial \theta}\,d\theta + \frac{\partial x}{\partial \phi}\,d\phi, \\ dy &= \frac{\partial y}{\partial r}\,dr + \frac{\partial y}{\partial \theta}\,d\theta + \frac{\partial y}{\partial \phi}\,d\phi \\ dz &= \frac{\partial z}{\partial r}\,dr + \frac{\partial z}{\partial \theta}\,d\theta + \frac{\partial z}{\partial \phi}\,d\phi \end{aligned}$$

which we can write in matrix form as

$$\begin{bmatrix} dx \\ dy \\ dz \end{bmatrix} = J \begin{bmatrix} dr \\ d\theta \\ d\phi \end{bmatrix},$$

where

$$J \equiv \frac{\partial(x,y,z)}{\partial(r,\theta,\phi)} = \begin{bmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{bmatrix} = \begin{bmatrix} \sin\theta\cos\phi & r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ \sin\theta\sin\phi & r\cos\theta\sin\phi & r\sin\theta\cos\phi \\ \cos\theta & -r\sin\theta & 0 \end{bmatrix}$$

is the Jacobian matrix for this transformation. The converse relation is given by

$$\begin{bmatrix} dr \\ d\theta \\ d\phi \end{bmatrix} = J^{-1} \begin{bmatrix} dx \\ dy \\ dz \end{bmatrix},$$

which implies that

$$\begin{bmatrix} \frac{\partial r}{\partial x} & \frac{\partial r}{\partial y} & \frac{\partial r}{\partial z} \\ \frac{\partial \theta}{\partial x} & \frac{\partial \theta}{\partial y} & \frac{\partial \theta}{\partial z} \\ \frac{\partial \phi}{\partial x} & \frac{\partial \phi}{\partial y} & \frac{\partial \phi}{\partial z} \end{bmatrix} = J^{-1}$$

This allows us to determine partial derivatives such as $\frac{\partial\theta}{\partial y}$ without explicitly invert the relations ($\star$). Inverting the matrix J yields

$$\begin{bmatrix} \frac{\partial r}{\partial x} & \frac{\partial r}{\partial y} & \frac{\partial r}{\partial z} \\ \frac{\partial \theta}{\partial x} & \frac{\partial \theta}{\partial y} & \frac{\partial \theta}{\partial z} \\ \frac{\partial \phi}{\partial x} & \frac{\partial \phi}{\partial y} & \frac{\partial \phi}{\partial z} \end{bmatrix} = \begin{bmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ \frac{1}{r}\cos\theta\cos\phi & \frac{1}{r}\cos\theta\sin\phi & -\frac{1}{r}\sin\theta \\ -\frac{1}{r}\frac{\sin\phi}{\sin\theta} & \frac{1}{r}\frac{\cos\phi}{\sin\theta} & 0 \end{bmatrix} \tag{5.2}$$

So, if we want to convert $\partial/\partial x$ to spherical coordinates, we first write

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi},$$

and then look at the identity (5.2) to extract

$$\frac{\partial r}{\partial x} = \sin\theta\cos\phi, \qquad \frac{\partial \theta}{\partial x} = \frac{1}{r}\cos\theta\cos\phi, \qquad \frac{\partial \phi}{\partial x} = -\frac{1}{r}\frac{\sin\phi}{\sin\theta}.$$

Replacing these in the previous expression, we obtain

$$\begin{aligned}\frac{\partial}{\partial x} &= \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} \\ &= \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial \theta} + \frac{1}{r}\cos\theta\frac{\partial}{\partial \phi}.\end{aligned}$$

Following a similar procedure, we also obtain

$$\begin{aligned}\frac{\partial}{\partial y} &= \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi} \\ &= \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial \theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial \phi}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial}{\partial z} &= \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi} \\ &= \cos\theta\,\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\,\frac{\partial}{\partial \theta}.\end{aligned}$$

Going back to the expression for each of the components $\hat{L}_{x,y,z}$, we get, for example:

$$\begin{aligned}\frac{i}{\hbar}\hat{L}_x &= y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \\ &= r\sin\theta\sin\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial \theta}\right) \\ &\qquad - r\cos\theta\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial \theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial \phi}\right) \\ &= -\sin\phi\frac{\partial}{\partial \theta} - \cot\theta\cos\phi\frac{\partial}{\partial \phi}.\end{aligned}$$

Proceed analogously to obtain the expressions for $\hat{L}_y$ and $\hat{L}_z$.

2. To minimize the chance for errors due to missing commutators of derivatives, keep in mind that "squaring" a differential operator means "apply it two times in a sequence, one after the other". When doing that, it is advisable to introduce a "test function" on which the operator will act. For example, when you need to determine $\hat{L}_x^2$, you can analyse what this operator does to an arbitrary function of θ and ϕ [say $f(\theta,\phi)$]. The first application of $\hat{L}_x$ to such function results in

$$\hat{L}_x\, f(\theta,\phi) = i\hbar\left[\sin\phi\frac{\partial\, f(\theta,\phi)}{\partial \theta} + \cot\theta\cos\phi\frac{\partial\, f(\theta,\phi)}{\partial \phi}\right] = g(\theta,\phi)$$

where $g(\theta,\phi)$ is the function generated by the action of $\hat{L}_x$ on $f(\theta,\phi)$. A subsequent application of the same operator leads to

$$\hat{L}_x^2\, f(\theta,\phi) = \hat{L}_x\left[\hat{L}_x f(\theta,\phi)\right] = \hat{L}_x\, g(\theta,\phi) = i\hbar\left[\sin\phi\frac{\partial\, g(\theta,\phi)}{\partial \theta} + \cot\theta\cos\phi\frac{\partial\, g(\theta,\phi)}{\partial \phi}\right].$$

When we now replace $g(\theta,\phi)$ found above, this becomes

$$
\begin{aligned}
-\hbar^{-2}\hat{L}_x^2\, f(\theta,\phi) &= \sin\phi\frac{\partial}{\partial\theta}\left[\sin\phi\frac{\partial\, f(\theta,\phi)}{\partial\theta} + \cot\theta\cos\phi\frac{\partial\, f(\theta,\phi)}{\partial\phi}\right] \\
&\quad + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\left[\sin\phi\frac{\partial\, f(\theta,\phi)}{\partial\theta} + \cot\theta\cos\phi\frac{\partial\, f(\theta,\phi)}{\partial\phi}\right] \\
&= \sin^2\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\theta^2} + \frac{\sin 2\phi}{2}\frac{\partial}{\partial\theta}\left(\cot\theta\frac{\partial\, f(\theta,\phi)}{\partial\phi}\right) \\
&\quad + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\left(\sin\phi\frac{\partial\, f(\theta,\phi)}{\partial\theta}\right) + \cos\phi\cot^2\theta\frac{\partial}{\partial\phi}\left(\cos\phi\frac{\partial\, f(\theta,\phi)}{\partial\phi}\right) \\
&= \sin^2\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\theta^2} + \frac{\sin 2\phi}{2}\left(-\csc^2\theta\frac{\partial\, f(\theta,\phi)}{\partial\phi} + \cot\theta\frac{\partial^2\, f(\theta,\phi)}{\partial\phi\partial\theta}\right) \\
&\quad + \cot\theta\cos\phi\left(\cos\phi\frac{\partial\, f(\theta,\phi)}{\partial\theta} + \sin\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\theta\partial\phi}\right) \\
&\quad + \cos\phi\cot^2\theta\left(-\sin\phi\frac{\partial\, f(\theta,\phi)}{\partial\phi} + \cos\phi\frac{\partial\, f(\theta,\phi)}{\partial^2\phi}\right) \\
&= \sin^2\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\theta^2} + \cos^2\phi\cot^2\theta\frac{\partial\, f(\theta,\phi)}{\partial^2\phi} \\
&\quad - \frac{\sin 2\phi}{2}\left(\csc^2\theta + \cot^2\theta\right)\frac{\partial\, f(\theta,\phi)}{\partial\phi} \\
&\quad + \cot\theta\sin 2\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\theta\partial\phi} + \cot\theta\cos^2\phi\frac{\partial\, f(\theta,\phi)}{\partial\theta}.
\end{aligned}
$$

Doing the same for $\hat{L}_y^2$ and $\hat{L}_z^2$ yields

$$
\begin{aligned}
-\hbar^{-2}\hat{L}_y^2\, f(\theta,\phi) &= \cos^2\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\theta^2} + \cot^2\theta\sin^2\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\phi^2} \\
&\quad + \frac{\sin 2\phi}{2}\left(\cot^2\theta + \csc^2\theta\right)\frac{\partial\, f(\theta,\phi)}{\partial\phi} \\
&\quad - \cot\theta\sin 2\phi\frac{\partial^2\, f(\theta,\phi)}{\partial\theta\partial\phi} + \cot\theta\sin^2\phi\frac{\partial\, f(\theta,\phi)}{\partial\theta}.
\end{aligned}
$$

and

$$
-\hbar^{-2}\hat{L}_z^2\, f(\theta,\phi) = \frac{\partial^2\, f(\theta,\phi)}{\partial\phi^2}.
$$

Adding the three results above we obtain

$$
\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right].
$$

3. We simply have to look at the last result and notice that $\hat{\boldsymbol{L}}^2$ is equal to the sum of all the θ- and ϕ-dependent terms in the Laplacian operator, except for the constant $\hbar^2$. Therefore, we can easily write

$$
\boldsymbol{\nabla}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left[\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hat{\boldsymbol{L}}^2}{r^2\hbar^2}.
$$

Problema 6 | Momento angular segundo uma direção arbitrária

Nas aulas foi afirmado que, quando é medida uma projeção do momento angular segundo qualquer direção no espaço, o resultado é um de entre $-l, -l+1, \ldots, l$ (em unidades de $\hbar$). Obviamente, é isto que esperamos ao medir $\hat{L}_z$ porque vimos que os seus valores próprios tomam precisamente esses valores. Vamos agora mostrar que os resultados possíveis numa medição segundo qualquer outra direção são os mesmos, considerando um exemplo.

Considere uma partícula com momento angular $l = 1$ e uma direção arbitrária no espaço definida pelo vetor unitário $\boldsymbol{n}$,

$$\boldsymbol{n} = \sin\alpha\cos\beta\,\boldsymbol{u}_x + \sin\alpha\sin\beta\,\boldsymbol{u}_y + \cos\alpha\,\boldsymbol{u}_z,$$

onde α, β são os ângulos polar e azimutal, respetivamente. Denotando a projeção de $\hat{\boldsymbol{L}}$ segundo a direção de $\boldsymbol{n}$ como $\hat{\boldsymbol{L}}_{\boldsymbol{n}}$,

$$\hat{\boldsymbol{L}}_{\boldsymbol{n}} \equiv \hat{\boldsymbol{L}} \cdot \boldsymbol{n} = \hat{L}_x \sin\alpha\cos\beta + \hat{L}_y \sin\alpha\sin\beta + \hat{L}_z\cos\alpha,$$

1. Mostre que podemos escrever
$$\hat{\boldsymbol{L}}_{\boldsymbol{n}} = \frac{1}{2}\sin\alpha e^{-i\beta}\hat{L}_+ + \frac{1}{2}\sin\alpha e^{i\beta}\hat{L}_- + \cos\alpha\hat{L}_z,$$
onde $\hat{L}_\pm$ são os operadores de escada para o momento angular.

2. Escreva a matriz que representa $\hat{\boldsymbol{L}}_{\boldsymbol{n}}$ na base dos autoestados de $\hat{L}^2$ e $\hat{L}_z$, ou seja, na base de estados $|l,m\rangle$ definida pelo conjunto $\big\{|1,1\rangle, |1,0\rangle, |1,-1\rangle\big\}$.

3. Partindo da matriz determinada na questão anterior, calcule os valores próprios de $\hat{\boldsymbol{L}}_{\boldsymbol{n}}$ e, desse modo, determine os resultados possíveis na medição desta observável.

Solution

1. Simply use the fact that
$$\hat{L}_x = \frac{\hat{L}_+ + \hat{L}_-}{2}, \qquad \hat{L}_y = \frac{\hat{L}_+ - \hat{L}_-}{2i}$$
and replace these two in the expression given for $\hat{L}_{\boldsymbol{n}}$.

2. To build that matrix we compute the action of $\hat{L}_{\boldsymbol{n}}$ on each of the basis kets, recalling that the action of the ladder operators and $\hat{L}_z$ on the kets $|l,m\rangle$ is
$$\hat{L}_\pm|l,m\rangle = \hbar\sqrt{l(l+1) - m(m\pm1)}\,|l,m\pm1\rangle, \qquad \hat{L}_z|l,m\rangle = m\hbar\,|l,m\rangle.$$
Using this, we have:
$$\hat{L}_{\boldsymbol{n}}|1,1\rangle = \frac{1}{2}\sin\alpha e^{i\beta}\hat{L}_-|1,1\rangle + \cos\alpha\hat{L}_z|1,1\rangle = \frac{\hbar}{\sqrt{2}}\sin\alpha e^{i\beta}|1,0\rangle + \hbar\cos\alpha|1,1\rangle$$
$$\hat{L}_{\boldsymbol{n}}|1,0\rangle = \frac{1}{2}\sin\alpha e^{-i\beta}\hat{L}_+|1,0\rangle + \frac{1}{2}\sin\alpha e^{i\beta}\hat{L}_-|1,0\rangle = \frac{\hbar}{\sqrt{2}}\sin\alpha e^{-i\beta}|1,1\rangle + \frac{\hbar}{\sqrt{2}}\sin\alpha e^{i\beta}|1,-1\rangle$$
$$\hat{L}_{\boldsymbol{n}}|1,-1\rangle = \frac{1}{2}\sin\alpha e^{-i\beta}\hat{L}_+|1,-1\rangle + \cos\alpha\hat{L}_z|1,1\rangle = \frac{\hbar}{\sqrt{2}}\sin\alpha e^{-i\beta}|1,0\rangle - \hbar\cos\alpha|1,1\rangle$$

From here we can determine every matrix element in the basis $\{|1,1\rangle, |1,0\rangle, |1,-1\rangle\}$. For example,

$$\langle 1,1|\hat{L}_{\boldsymbol{n}}|1,1\rangle = \hbar\cos\alpha, \quad \langle 1,0|\hat{L}_{\boldsymbol{n}}|1,1\rangle = \frac{\hbar}{\sqrt{2}}\sin\alpha e^{i\beta}, \quad \langle 1,0|\hat{L}_{\boldsymbol{n}}|1,1\rangle = 0.$$

These 3 matrix elements define the 1st column of the matrix representation of $\hat{L}_{\boldsymbol{n}}$. The complete matrix is

$$\hat{L}_{\boldsymbol{n}} \mapsto \hbar \begin{bmatrix} \cos\alpha & \frac{\sin\alpha}{\sqrt{2}}e^{-i\beta} & 0 \\ \frac{\sin\alpha}{\sqrt{2}}e^{i\beta} & 0 & \frac{\sin\alpha}{\sqrt{2}}e^{-i\beta} \\ 0 & \frac{\sin\alpha}{\sqrt{2}}e^{i\beta} & -\cos\alpha \end{bmatrix}, \qquad \text{basis } \{|1,1\rangle, |1,0\rangle, |1,-1\rangle\}.$$

3. The eigenvalues of the matrix above follow directly from (putting $\hbar \to 1$ temporarily)

$$\begin{vmatrix} \cos\alpha - \lambda & \frac{\sin\alpha}{\sqrt{2}}e^{-i\beta} & 0 \\ \frac{\sin\alpha}{\sqrt{2}}e^{i\beta} & -\lambda & \frac{\sin\alpha}{\sqrt{2}}e^{-i\beta} \\ 0 & \frac{\sin\alpha}{\sqrt{2}}e^{i\beta} & -\cos\alpha - \lambda \end{vmatrix} = 0 \qquad \Leftrightarrow \qquad \lambda = -1,\, 0,\, 1.$$

Restoring the prefactor of the matrix, $\hbar$, the three eigenvalues are $\{-\hbar, 0, \hbar\}$. We note that these eigenvalues are totally independent of the angles α and β. Consequently, a single measurement of $\hat{L}_{\boldsymbol{n}}$ always gives one of $\{-\hbar, 0, \hbar\}$, independently of the direction $\boldsymbol{n}$ along which we are measuring the angular momentum. In particular, a measurement of $\hat{L}_x$, $\hat{L}_y$, or $\hat{L}_z$ can only yield one of these three values for a particle in a state with $l = 1$.
