11. Find a solution to the eigenvalue problem for the operator \hat{L}^2 (Derive!)

We write it as

$$\hat{L}^2 Y_\beta(\theta,\phi) = \hbar^2 \beta Y_\beta(\theta,\phi),$$

where the eigenvalue we try to find is denoted β . Since $Y_{\beta}(\theta, \phi)$ is at the same time an eigenfunction of \hat{L}_z (which we have already found), we represent

$$Y_{\beta}(\theta,\phi) = \frac{1}{\sqrt{2\pi}} P_{\beta}^{m}(\theta) e^{im\phi}$$

If we use the direct expression of \hat{L}^2 , namely

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right],$$

we get

$$-\hbar^2 \left[\frac{1}{\sin \theta} \partial_\theta (\sin \theta \, \partial_\theta) + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right] Y_\beta = \hbar^2 \,\beta \, Y_\beta.$$

After substituting $Y_{\beta} = (1/\sqrt{2\pi})P_{\beta}^{m}(\theta)e^{im\phi}$ and dividing out the $e^{im\phi}$, one obtains for $P_{\beta}^{m}(\theta)$:

$$\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d}{d\theta}\right) - \frac{m^2}{\sin^2\theta}\right]P^m_\beta(\theta) = -\beta\,P^m_\beta(\theta).$$

This is the associated Legendre equation. Regular (single-valued, finite) so-lutions on $0 \leq \theta \leq \pi$ exist only if?

$$\beta = l(l+1), \quad l = 0, 1, 2, \dots, \quad |m| \le l,$$
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in which case

$$P^m_\beta(\theta) \to P^m_l(\cos\theta)$$

and the full eigenfunctions are the spherical harmonics

$$Y_l^m(\theta,\phi) = N_l^m P_l^m(\cos\theta) \, \frac{e^{im\phi}}{\sqrt{2\pi}}.$$

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16. How, in quantum mechanics, can one calculate the angle θ between the angular momentum vector L and the z-axis? Calculate θ for the 3d orbitals (l = 2) with magnetic quantum numbers m = -2 and m = +1.

In a simultaneous eigenstate $|l, m\rangle$ we have

$$\langle L^2 \rangle = \hbar^2 l(l+1), \qquad \langle L_z \rangle = m\hbar.$$

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If we picture **L** as a vector of length $\sqrt{\langle L^2 \rangle} = \hbar \sqrt{l(l+1)}$ and z-component $\langle L_z \rangle = m\hbar$, then the angle θ it makes with the z-axis satisfies

$$\cos \theta = \frac{\langle L_z \rangle}{\sqrt{\langle L^2 \rangle}} = \frac{m\hbar}{\hbar\sqrt{l(l+1)}} = \frac{m}{\sqrt{l(l+1)}}.$$

Hence

$$\theta = \arccos\left(\frac{m}{\sqrt{l(l+1)}}\right).$$

For the 3d orbitals, l = 2 so $\sqrt{l(l+1)} = \sqrt{6}$. Thus

$$\theta_{m=-2} = \arccos\left(\frac{-2}{\sqrt{6}}\right) \approx 145.8^{\circ}, \qquad \theta_{m=+1} = \arccos\left(\frac{1}{\sqrt{6}}\right) \approx 65.9^{\circ}.$$

22. What does the equation for the radial wave function look like if we assume that the electron is an uncharged particle and moves around the nucleus in an orbit with a fixed radius (r=const)?

Starting from the general time-independent Schrödinger equation in a central potential U(r),

$$-\frac{\hbar^2}{2M}\Delta\psi(\mathbf{r}) + U(r)\,\psi(\mathbf{r}) = E\,\psi(\mathbf{r}),$$

and using the spherical-coordinate form of the Laplacian,

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2},$$

we write $\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi)$. Since $\hat{L}^2 Y_l^m = \hbar^2 l(l+1) Y_l^m$, the radial equation (cf. §10.2–10.3) becomes

$$-\frac{\hbar^2}{2M}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{l(l+1)}{r^2}R\right] + U(r)R = ER.$$

If the electron is "uncharged," we set U(r) = 0. Thus

$$-\frac{\hbar^2}{2M} \left[R''(r) + \frac{2}{r} R'(r) - \frac{l(l+1)}{r^2} R(r) \right] = E R(r).$$

Finally, if the radius is fixed at $r = R_0 = \text{const}$, there is no radial dependence: $R'(R_0) = R''(R_0) = 0$. The only surviving term is the centrifugal one, yielding

$$\frac{\hbar^2 l(l+1)}{2M R_0^2} R(R_0) = E R(R_0) \implies E = \frac{\hbar^2 l(l+1)}{2M R_0^2},$$
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and the "radial" wave function may be represented (up to normalization) by

$$R(r) \propto \delta(r - R_0)$$

36. How looks like the electron configuration for Li, Na and K atoms? Why? What do all these materials have in common (in terms of physical properties)? How does this relate to the configuration of the electrons?

Li (Z=3):
$$1s^2 2s^1$$
,
Na (Z=11): $1s^2 2s^2 2p^6 3s^1$,
K (Z=19): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.

By the Aufbau principle, electrons fill lowest-energy orbitals first, and each of these atoms has a noble-gas core plus one electron in an ns orbital (n = 2, 3, 4 respectively).

Common physical properties:

- Soft, silvery metals that are easily cut.
- Low melting and boiling points compared to most metals.
- Excellent electrical and thermal conductors.
- Very reactive, especially with water, forming M^+ ions and releasing hydrogen.
- All form +1 cations in compounds.

Each has a single valence electron in an s orbital outside a closed shell. That lone ns^1 electron is held relatively weakly (low ionization energy), so it is easily lost to form M^+ . This one-electron-in-an-outer-shell structure underlies their shared metallic character and high chemical reactivity. 42.Can you prove the following expression (page 127): "In the first order approximation of λ the coefficient $a_n^{(1)}$ must satisfy $a_n^{(1)} + (a_n^{(1)})^* = 0$

The perturbed wavefunction expanded to first order in λ :

$$\Psi_n = \Psi_n^{(0)} + \lambda \, \Psi_n^{(1)} + O(\lambda^2), \quad \Psi_n^{(1)} = \sum_m a_m^{(1)} \, \Psi_m^{(0)}.$$

Normalization demands

$$\int \Psi_n^*(\mathbf{r}) \, \Psi_n(\mathbf{r}) \, d\tau = 1.$$

Substitute the expansion and keep only terms up to order λ :

$$\int \Psi_n^* \Psi_n \, d\tau = \int \left[\Psi_n^{(0)*} + \lambda \, \Psi_n^{(1)*} \right] \left[\Psi_n^{(0)} + \lambda \, \Psi_n^{(1)} \right] \, d\tau + O(\lambda^2)$$
$$= \int \left| \Psi_n^{(0)} \right|^2 \, d\tau + \lambda \int \left[\Psi_n^{(0)*} \, \Psi_n^{(1)} + \Psi_n^{(1)*} \, \Psi_n^{(0)} \right] \, d\tau + O(\lambda^2).$$

We know $\{\Psi_m^{(0)}\}$ is orthonormal, so

$$\int \Psi_n^{(0)*} \Psi_n^{(0)} d\tau = 1, \qquad \int \Psi_n^{(0)*} \Psi_m^{(0)} d\tau = 0 \quad (m \neq n).$$

Next, substitute $\Psi_n^{(1)} = \sum_m a_m^{(1)} \Psi_m^{(0)}$ into the first-order integral:

$$\int \Psi_n^{(0)*} \Psi_n^{(1)} d\tau = \sum_m a_m^{(1)} \int \Psi_n^{(0)*} \Psi_m^{(0)} d\tau = a_n^{(1)},$$
$$\int \Psi_n^{(1)*} \Psi_n^{(0)} d\tau = \sum_m (a_m^{(1)})^* \int \Psi_m^{(0)*} \Psi_n^{(0)} d\tau = (a_n^{(1)})^*.$$

Therefore the normalization condition becomes

$$1 = 1 + \lambda \left[a_n^{(1)} + (a_n^{(1)})^* \right] + O(\lambda^2).$$

For this to hold at order λ , the coefficient must vanish:

$$a_n^{(1)} + \left(a_n^{(1)}\right)^* = 0.$$

Thus $a_n^{(1)}$ is purely imaginary, as required.