Complement H_{XI}

EXERCISES

1. A particle of mass m is placed in an infinite one-dimensional well of width a:

$V(x) = 0$ for $0 \leqslant x \leqslant a$

$V(x) = +\infty$ everywhere else

It is subject to a perturbation W of the form:

$$W(x) = aw_0\,\delta\left(x - \frac{a}{2}\right)$$

where w_0 is a real constant with the dimensions of an energy.

a. Calculate, to first order in w_0, the modifications induced by $W(x)$ in the energy levels of the particle.

b. Actually, the problem is exactly soluble. Setting $k = \sqrt{2mE/\hbar^2}$, show that the possible values of the energy are given by one of the two equations $\sin(ka/2) = 0$ or $\tan(ka/2) = -\hbar^2 k/maw_0$ (as in exercise 2 of complement L_I, watch out for the discontinuity of the derivative of the wave function at $x = a/2$).

Discuss the results obtained with respect to the sign and size of w_0. In the limit $w_0 \longrightarrow 0$, show that one obtains the results of the preceding question.

2. Consider a particle of mass m placed in an infinite two-dimensional potential well of width a (*cf.* complement G_{II}):

$V(x, y) = 0$ if $0 \leqslant x \leqslant a$ and $0 \leqslant y \leqslant a$

$V(x, y) = +\infty$ everywhere else

This particle is also subject to a perturbation W described by the potential:

$$W(x, y) = w_0 \quad \text{for} \quad 0 \leqslant x \leqslant \frac{a}{2} \quad \text{and} \quad 0 \leqslant y \leqslant \frac{a}{2}$$

$W(x, y) = 0$ everywhere else

a. Calculate, to first order in w_0, the perturbed energy of the ground state.

b. Same question for the first excited state. Give the corresponding wave functions to zeroeth order in w_0.

3. A particle of mass m, constrained to move in the xOy plane, has a Hamiltonian:

$$H_0 = \frac{P_x^2}{2m} + \frac{P_y^2}{2m} + \frac{1}{2} m\omega^2(X^2 + Y^2)$$

(a two-dimensional harmonic oscillator, of angular frequency ω). We want to study the effect on this particle of a perturbation W given by:

$$W = \lambda_1 W_1 + \lambda_2 W_2$$

where λ_1 and λ_2 are constants, and the expressions for W_1 and W_2 are:

$$W_1 = m\omega^2 XY$$
$$W_2 = \hbar\omega\left(\frac{L_z^2}{\hbar^2} - 2\right)$$

(L_z is the component along Oz of the orbital angular momentum of the particle).

In the perturbation calculations, consider only the corrections to first order for the energies and to zeroeth order for the state vectors.

a. Indicate without calculations the eigenvalues of H_0, their degrees of degeneracy and the associated eigenvectors.

In what follows, consider only the second excited state of H_0, of energy $3\hbar\omega$ and which is three-fold degenerate.

b. Calculate the matrices representing the restrictions of W_1 and W_2 to the eigensubspace of the eigenvalue $3\hbar\omega$ of H_0.

c. Assume $\lambda_2 = 0$ and $\lambda_1 \ll 1$.

Calculate, using perturbation theory, the effect of the term $\lambda_1 W_1$ on the second excited state of H_0.

d. Compare the results obtained in *c* with the limited expansion of the exact solution, to be found with the help of the methods described in complement H_V (normal vibrational modes of two coupled harmonic oscillators).

e. Assume $\lambda_2 \ll \lambda_1 \ll 1$. Considering the results of question *c* to be a new unperturbed situation, calculate the effect of the term $\lambda_2 W_2$.

f. Now assume that $\lambda_1 = 0$ and $\lambda_2 \ll 1$.

Using perturbation theory, find the effect of the term $\lambda_2 W_2$ on the second excited state of H_0.

g. Compare the results obtained in *f* with the exact solution, which can be found from the discussions of complement D_{VI}.

h. Finally, assume that $\lambda_1 \ll \lambda_2 \ll 1$. Considering the results of question *f* to be a new unperturbed situation, calculate the effect of the term $\lambda_1 W_1$.

4. Consider a particle P of mass μ, constrained to move in the xOy plane in a circle centered at O with fixed radius ρ (a two-dimensional rotator). The only variable of the system is the angle $\alpha = (Ox, OP)$, and the quantum state of the particle is defined by the wave function $\psi(\alpha)$ (which represents the probability amplitude of finding the particle at the point of the circle fixed by the angle α). At each point of the circle, $\psi(\alpha)$ can take on only one value, so that:

$$\psi(\alpha + 2\pi) = \psi(\alpha)$$

$\psi(\alpha)$ is normalized if:

$$\int_0^{2\pi} |\psi(\alpha)|^2 \, d\alpha = 1$$

a. Consider the operator $M = \frac{\hbar}{i} \frac{d}{d\alpha}$. Is M Hermitian? Calculate the eigenvalues and normalized eigenfunctions of M. What is the physical meaning of M?

b. The kinetic energy of the particle can be written:

$$H_0 = \frac{M^2}{2\mu\rho^2}$$

Calculate the eigenvalues and eigenfunctions of H_0. Are the energies degenerate?

c. At $t = 0$, the wave function of the particle is $N \cos^2 \alpha$ (where N is a normalization coefficient). Discuss the localization of the particle on the circle at a subsequent time t.

d. Assume that the particle has a charge q and that it interacts with a uniform electric field $\mathscr{E}$ parallel to Ox. We must therefore add to the Hamiltonian H_0 the perturbation:

$$W = -q\mathscr{E}\rho \cos \alpha$$

Calculate the new wave function of the ground state to first order in $\mathscr{E}$. Determine the proportionality coefficient χ (the linear suceptibility) between the electric dipole parallel to Ox acquired by the particle and the field $\mathscr{E}$.

e. Consider, for the ethane molecule CH_3-CH_3, a rotation of one CH_3 group relative to the other about the straight line joining the two carbon atoms.

To a first approximation, this rotation is free, and the Hamiltonian H_0 introduced in *b* describes the rotational kinetic energy of one of the CH_3 groups relative to the other ($2\mu\rho^2$ must, however, be replaced by λI, where I is the moment of inertia of the CH_3 group with respect to the rotational axis and λ is a constant). To take

account of the electrostatic interaction energy between the two CH_3 groups, we add to H_0 a term of the form:

$$W = b \cos 3\alpha$$

where b is a real constant.

Give a physical justification for the α-dependence of W. Calculate the energy and wave function of the new ground state (to first order in b for the wave function and to second order for the energy). Give a physical interpretation of the result.

5. Consider a system of angular momentum **J**. We confine ourselves in this exercise to a three-dimensional subspace, spanned by the three kets $|+1\rangle$, $|0\rangle$, $|-1\rangle$, common eigenstates of $\mathbf{J}^2$ (eigenvalue $2\hbar^2$) and J_z (eigenvalues $+\hbar, 0, -\hbar$). The Hamiltonian H_0 of the system is:

$$H_0 = aJ_z + \frac{b}{\hbar} J_z^2$$

where a and b are two positive constants, which have the dimensions of an angular frequency.

a. What are the energy levels of the system? For what value of the ratio b/a is there degeneracy?

b. A static field $\mathbf{B}_0$ is applied in a direction **u** with polar angles θ and φ. The interaction with $\mathbf{B}_0$ of the magnetic moment of the system:

$$\mathbf{M} = \gamma \mathbf{J}$$

(γ : the gyromagnetic ratio, assumed to be negative) is described by the Hamiltonian:

$$W = \omega_0 J_u$$

where $\omega_0 = -\gamma |\mathbf{B}_0|$ is the Larmor angular frequency in the field $\mathbf{B}_0$, and J_u is the component of **J** in the **u** direction:

$$J_u = J_z \cos\theta + J_x \sin\theta \cos\varphi + J_y \sin\theta \sin\varphi$$

Write the matrix which represents W in the basis of the three eigenstates of H_0.

c. Assume that $b = a$ and that the **u** direction is parallel to Ox. We also have $\omega_0 \ll a$.

Calculate the energies and eigenstates of the system, to first order in ω_0 for the energies and to zeroeth order for the eigenstates.

d. Assume that $b = 2a$ and that we again have $\omega_0 \ll a$, the direction of **u** now being arbitrary.

In the $\{|+1\rangle, |0\rangle, |-1\rangle\}$ basis, what is the expansion of the ground state $|\psi_0\rangle$ of $H_0 + W$, to first order in ω_0?

Calculate the mean value $\langle \mathbf{M} \rangle$ of the magnetic moment $\mathbf{M}$ of the system in the state $|\psi_0\rangle$. Are $\langle \mathbf{M} \rangle$ and $\mathbf{B}_0$ parallel?

Show that one can write:

$$\langle M_i \rangle = \sum_j \chi_{ij} B_j$$

with $i, j = x, y, z$. Calculate the coefficients χ_{ij} (the components of the susceptibility tensor).

6. Consider a system formed by an electron spin $\mathbf{S}$ and two nuclear spins $\mathbf{I}_1$ and $\mathbf{I}_2$ ($\mathbf{S}$ is, for example, the spin of the unpaired electron of a paramagnetic diatomic molecule, and $\mathbf{I}_1$ and $\mathbf{I}_2$ are the spins of the two nuclei of this molecule).

Assume that $\mathbf{S}, \mathbf{I}_1, \mathbf{I}_2$ are all spin 1/2's. The state space of the three-spin system is spanned by the eight orthonormal kets $|\varepsilon_S, \varepsilon_1, \varepsilon_2\rangle$, common eigenvectors of S_z, I_{1z}, I_{2z}, with respective eigenvalues $\varepsilon_S\hbar/2$, $\varepsilon_1\hbar/2$, $\varepsilon_2\hbar/2$ (with $\varepsilon_S = \pm$, $\varepsilon_1 = \pm$, $\varepsilon_2 = \pm$). For example, the ket $|+, -, +\rangle$ corresponds to the eigenvalues $+\hbar/2$ for S_z, $-\hbar/2$ for I_{1z}, and $+\hbar/2$ for I_{2z}.

a. We begin by neglecting any coupling of the three spins. We assume, however, that they are placed in a uniform magnetic field $\mathbf{B}$ parallel to Oz. Since the gyromagnetic ratios of $\mathbf{I}_1$ and $\mathbf{I}_2$ are equal, the Hamiltonian H_0 of the system can be written:

$$H_0 = \Omega S_z + \omega I_{1z} + \omega I_{2z}$$

where Ω and ω are real, positive constants, proportional to $|\mathbf{B}|$. Assume $\Omega > 2\omega$.

What are the possible energies of the three-spin system and their degrees of degeneracy? Draw the energy diagram.

b. We now take coupling of the spins into account by adding the Hamiltonian:

$$W = a\,\mathbf{S} \cdot \mathbf{I}_1 + a\,\mathbf{S} \cdot \mathbf{I}_2$$

where a is a real, positive constant (the direct coupling of $\mathbf{I}_1$ and $\mathbf{I}_2$ is negligible).

What conditions must be satisfied by $\varepsilon_S, \varepsilon_1, \varepsilon_2, \varepsilon'_S, \varepsilon'_1, \varepsilon'_2$ for $a\mathbf{S} \cdot \mathbf{I}_1$ to have a non-zero matrix element between $|\varepsilon_S, \varepsilon_1, \varepsilon_2\rangle$ and $|\varepsilon'_S, \varepsilon'_1, \varepsilon'_2\rangle$? Same question for $a\,\mathbf{S} \cdot \mathbf{I}_2$.

c. Assume that:

$$a\hbar^2 \ll \hbar\Omega, \hbar\omega$$

so that W can be treated like a perturbation with respect to H_0. To first order in W, what are the eigenvalues of the total Hamiltonian $H = H_0 + W$? To zeroeth order in W, what are the eigenstates of H? Draw the energy diagram.

d. Using the approximation of the preceding question, determine the Bohr frequencies which can appear in the evolution of $\langle S_x \rangle$ when the coupling W of the spins is taken into account.

In an E.P.R. (Electronic Paramagnetic Resonance) experiment, the frequencies of the resonance lines observed are equal to the preceding Bohr frequencies. What is the shape of the E.P.R. spectrum observed for the three-spin system? How can the coupling constant a be determined from this spectrum?

e. Now assume that the magnetic field **B** is zero, so that $\Omega = \omega = 0$. The Hamiltonian then reduces to W.

α. Let $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$ be the total nuclear spin. What are the eigenvalues of $\mathbf{I}^2$ and their degrees of degeneracy? Show that W has no matrix elements between eigenstates of $\mathbf{I}^2$ of different eigenvalues.

β. Let $\mathbf{J} = \mathbf{S} + \mathbf{I}$ be the total spin. What are the eigenvalues of $\mathbf{J}^2$ and their degrees of degeneracy? Determine the energy eigenvalues of the three-spin system and their degrees of degeneracy. Does the set $\{ \mathbf{J}^2, J_z \}$ form a C.S.C.O.? Same question for $\{ \mathbf{I}^2, \mathbf{J}^2, J_z \}$.

7. Consider a nucleus of spin $I = 3/2$, whose state space is spanned by the four vectors $|m\rangle$ ($m = +3/2, +1/2, -1/2, -3/2$), common eigenvectors of $\mathbf{I}^2$ (eigenvalue $15\hbar^2/4$) and I_z (eigenvalue $m\hbar$).

This nucleus is placed at the coordinate origin in a non-uniform electric field derived from a potential $U(x, y, z)$. The directions of the axes are chosen such that, at the origin:

$$\frac{\partial^2 U}{\partial x\, \partial y} = \frac{\partial^2 U}{\partial y\, \partial z} = \frac{\partial^2 U}{\partial z\, \partial x} = 0$$

Recall that U satisfies Laplace's equation:

$$\Delta U = 0$$

We shall assume that the interaction Hamiltonian between the electric field gradient at the origin and the electric quadrupole moment of the nucleus can be written:

$$H_0 = \frac{qQ}{2I(2I-1)\hbar^2} \frac{1}{\hbar^2} [a_x I_x^2 + a_y I_y^2 + a_z I_z^2]$$

where q is the electron charge, Q is a constant with the dimensions of a surface and proportional to the quadrupole moment of the nucleus, and:

$$a_x = \left(\frac{\partial^2 U}{\partial x^2}\right)_0 \quad ; \quad a_y = \left(\frac{\partial^2 U}{\partial y^2}\right)_0 \quad ; \quad a_z = \left(\frac{\partial^2 U}{\partial z^2}\right)_0$$

(the index 0 indicates that the derivatives are evaluated at the origin).

a. Show that, if U is symmetrical with respect to revolution about Oz, H_0 has the form:

$$H_0 = A[3I_z^2 - I(I+1)\hbar^2]$$

where A is a constant to be specified. What are the eigenvalues of H_0, their degrees of degeneracy and the corresponding eigenstates?

b. Show that, in the general case, H_0 can be written:

$$H_0 = A[3I_z^2 - I(I+1)\hbar^2] + B(I_+^2 + I_-^2)$$

where A and B are constants, to be expressed in terms of a_x and a_y.

What is the matrix which represents H_0 in the $\{ | m \rangle \}$ basis? Show that it can be broken down into two 2×2 submatrices. Determine the eigenvalues of H_0 and their degrees of degeneracy, as well as the corresponding eigenstates.

c. In addition to its quadrupole moment, the nucleus has a magnetic moment $\mathbf{M} = \gamma \mathbf{I}$ (γ: the gyromagnetic ratio). Onto the electrostatic field is superposed a magnetic field $\mathbf{B}_0$, of arbitrary direction $\mathbf{u}$. We set $\omega_0 = -\gamma |\mathbf{B}_0|$.

What term W must be added to H_0 in order to take into account the coupling between $\mathbf{M}$ and $\mathbf{B}_0$? Calculate the energies of the system to first order in B_0.

d. Assume $\mathbf{B}_0$ to be parallel to Oz and weak enough for the eigenstates found in *b* and the energies to first order in ω_0 found in *c* to be good approximations.

What are the Bohr frequencies which can appear in the evolution of $\langle I_x \rangle$? Deduce from them the shape of the nuclear magnetic resonance spectrum which can be observed with a radiofrequency field oscillating along Ox.

8. A particle of mass m is placed in an infinite one-dimensional potential well of width a:

$$\begin{cases} V(x) = 0 & \text{for } 0 \leqslant x \leqslant a \\ V(x) = +\infty & \text{elsewhere} \end{cases}$$

Assume that this particle, of charge $-q$, is subject to a uniform electric field $\mathscr{E}$, with the corresponding perturbation W being:

$$W = q\mathscr{E}\left(X - \frac{a}{2}\right)$$

a. Let ε_1 and ε_2 be the corrections to first- and second-order in $\mathscr{E}$ for the ground state energy.

Show that ε_1 is zero. Give the expression for ε_2 in the form of a series, whose terms are to be calculated in terms of q, $\mathscr{E}$, m, a, $\hbar$ (the integrals given at the end of the exercise can be used).

b. By finding upper bounds for the terms of the series for ε_2, give an upper bound for ε_2 (*cf.* §B-2-c of chapter XI). Similarly, give a lower bound ε_2, obtained by retaining only the principal term of the series.

With what accuracy do the two preceding bounds enable us to bracket the exact value of the shift ΔE in the ground state to second order in $\mathscr{E}$?

c. We now want to calculate the shift ΔE by using the variational method. Choose as a trial function:

$$\psi_\alpha(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)\left[1 + \alpha q \mathscr{E}\left(x - \frac{a}{2}\right)\right]$$

where α is the variational parameter. Explain this choice of trial functions.

Calculate the mean energy $\langle H \rangle(\alpha)$ of the ground state to second order in $\mathscr{E}$ [assuming the expansion of $\langle H \rangle(\alpha)$ to second order in $\mathscr{E}$ to be sufficient]. Determine the optimal value of α. Find the result ΔE_{var} given by the variational method for the shift in the ground state to second order in $\mathscr{E}$.

By comparing ΔE_{var} with the results of *b*, evaluate the accuracy of the variational method applied to this example.

We give the integrals:

$$\frac{2}{a}\int_0^a \left(x - \frac{a}{2}\right) \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2n\pi x}{a}\right) dx = -\frac{16na}{\pi^2} \frac{1}{(1 - 4n^2)^2}$$

$n = 1, 2, 3, \ldots$

$$\frac{2}{a}\int_0^a \left(x - \frac{a}{2}\right)^2 \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{a^2}{2}\left(\frac{1}{6} - \frac{1}{\pi^2}\right)$$

$$\frac{2}{a}\int_0^a \left(x - \frac{a}{2}\right) \sin\left(\frac{\pi x}{a}\right) \cos\left(\frac{\pi x}{a}\right) dx = -\frac{a}{2\pi}$$

For all the numerical calculations, take $\pi^2 = 9.87$.

9. We want to calculate the ground state energy of the hydrogen atom by the variational method, choosing as trial functions the spherically symmetrical functions $\varphi_\alpha(\mathbf{r})$ whose r-dependence is given by:

$$\begin{cases} \varphi_\alpha(r) = C\left(1 - \dfrac{r}{\alpha}\right) & \text{for } r \leqslant \alpha \\ \varphi_\alpha(r) = 0 & \text{for } r > \alpha \end{cases}$$

C is a normalization constant and α is the variational parameter.

a. Calculate the mean value of the kinetic and potential energies of the electron in the state $|\varphi_\alpha\rangle$. Express the mean value of the kinetic energy in terms

of $\nabla\varphi$, so as to avoid the "delta functions" which appear in $\Delta\varphi$ (since $\nabla\varphi$ is discontinuous).

b. Find the optimal value α_0 of α. Compare α_0 with the Bohr radius a_0.

c. Compare the approximate value obtained for the ground state energy with the exact value $-E_I$.

10. We intend to apply the variational method to the determination of the energies of a particle of mass m in an infinite potential well:

$$V(x) = 0 \qquad -a \leqslant x \leqslant a$$
$$V(x) = \infty \qquad \text{everywhere else}$$

a. We begin by approximating, in the interval $[-a, +a]$, the wave function of the ground state by the simplest even polynomial which goes to zero at $x = \pm a$:

$$\psi(x) = a^2 - x^2 \qquad \text{for} \quad -a \leqslant x \leqslant a$$
$$\psi(x) = 0 \qquad \text{everywhere else}$$

(a variational family reduced to a single trial function).

Calculate the mean value of the Hamiltonian H in this state. Compare the result obtained with the true value.

b. Enlarge the family of trial functions by choosing an even fourth-degree polynomial which goes to zero at $x = \pm a$:

$$\psi_\alpha(x) = (a^2 - x^2)(a^2 - \alpha x^2) \qquad \text{for} \quad -a \leqslant x \leqslant a$$
$$\psi_\alpha(x) = 0 \qquad \text{everywhere else}$$

(a variational family depending on the real parameter α).

(α) Show that the mean value of H in the state $\psi_\alpha(x)$ is:

$$\langle H \rangle(\alpha) = \frac{\hbar^2}{2ma^2} \frac{33\alpha^2 - 42\alpha + 105}{2\alpha^2 - 12\alpha + 42}$$

(β) Show that the values of α which minimize or maximize $\langle H \rangle(\alpha)$ are given by the roots of the equation:

$$13\alpha^2 - 98\alpha + 21 = 0$$

(γ) Show that one of the roots of this equation gives, when substituted into $\langle H \rangle(\alpha)$, a value of the ground state energy which is much more precise than the one obtained in *a*.

(δ) What other eigenvalue is approximated when the second root of the equation obtained in *b*-β is used? Could this have been expected? Evaluate the precision of this determination.

c. Explain why the simplest polynomial which permits the approximation of the first excited state wave function is $x(a^2 - x^2)$.

What approximate value is then obtained for the energy of this state?