Complement H_{XI}

EXERCISES

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

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

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}):

$$V(x, y) = 0 \qquad \text{if} \quad 0 \leqslant x \leqslant a \quad \text{and} \quad 0 \leqslant y \leqslant a$$
$$V(x, y) = +\infty \quad \text{everywhere else}$$

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

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

$$W(x, y) = 0 \quad \text{everywhere else}$$

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.

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:

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

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

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

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

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:

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

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 $x = \pm a$:

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

(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 $x = \pm a$:

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

(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?

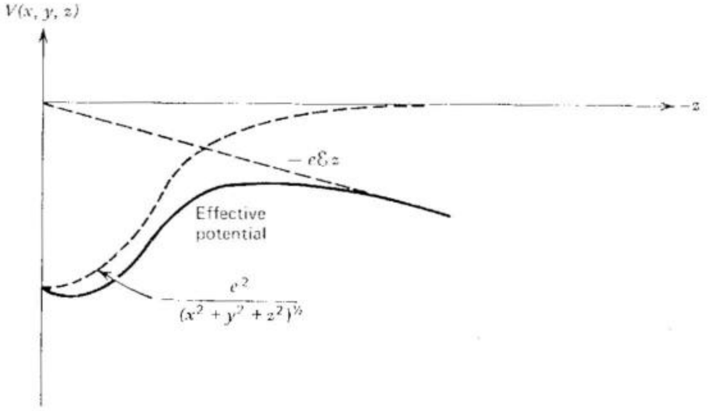

Fig. 16-2. Schematic picture of potential energy as a function of z with x and y held fixed. The dotted line represents the Coulomb potential, the dashed line the potential energy due to the external field, and the solid line the total potential.

however, they may be stable on a time scale of the age of the universe,[4] and hence the observations agree perfectly with what the first few terms of the perturbation series predict.

Problems

1. Consider the hydrogen atom, and assume that the proton, instead of being a point-source of the Coulomb field, is a uniformly charged sphere of radius R, so that the Coulomb potential is now modified to

$$\begin{aligned} V(r) &= -\frac{3e^2}{2R^3}\left(R^2 - \frac{1}{3}r^2\right) & r &< R(\ll a_0) \\ &= -\frac{e^2}{r} & r &> R \end{aligned}$$

Calculate the energy shift for the $n = 1$, $l = 0$ state, and for the $n = 2$ states, caused by this modification, using the wave functions given in (12-25).

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[4] Actually a simple barrier penetration calculation of the type carried out in Chapter 5 shows that the time scale is more like 10^{1000} lifetimes of the universe, for fairly reasonable fields!

2. Calculate the energy shift in the ground state of the one-dimensional harmonic oscillator, when the perturbation

$$V = \lambda x^4$$

is added to

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

3. Consider a square well in one dimension. If the edges of the well are rounded off as shown in the figure, what is the change in the ground state energy? Choose your rounding-off parametrization such that $\int_{-\infty}^{\infty} V(x)\,dx$ remains unchanged.

4. The bottom of an infinite well is changed to have the shape

$$V(x) = \epsilon \sin\frac{\pi x}{b} \qquad 0 \leq x \leq b$$

Calculate the energy shifts for all the excited states to first order in ϵ. Note that the well originally had $V(x) = 0$ for $0 \leq x \leq b$, with $V = \infty$ elsewhere.

5. Prove the sum rule (Thomas-Reiche-Kuhn sum rule)

$$\sum_n (E_n - E_a)|\langle n|x|a\rangle|^2 = \frac{\hbar^2}{2m}$$

[*Hint.* (a) Write the commutation relation $[p,x] = \hbar/i$ in the form

$$\sum_n \left\{ \langle a|p|n\rangle\langle n|x|a\rangle - \langle a|x|n\rangle\langle n|p|a\rangle \right\} = \frac{\hbar}{i}\langle a|a\rangle = \frac{\hbar}{i}$$

(b) Use the fact that

$$\langle a|p|n\rangle = \left\langle a\middle| m\frac{dx}{dt}\middle|n\right\rangle = m\frac{i}{\hbar}\langle a|[H,x]|n\rangle$$

in working out the problem.]

6. Check the above sum rule for the one-dimensional harmonic oscillator, with "a" taken in the ground state.

7. Work out the first order Stark effect in the $n = 3$ state of the hydrogen atom. Do not bother to work out all the integrals.

8. Consider an electron in a state n in a hydrogen atom. The atom is placed

in an external electric field $\mathcal{E}$. Estimate the lifetime of the atom, or, equivalently, the transmission coefficient through the barrier made up of the Colulomb attraction to the nucleus. It is enough to consider a one-dimensional model of the problem.

9. Consider a two-dimensional harmonic oscillator described by the Hamiltonian

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

Generalize the approach of Chapter 7 to obtain solutions of this problem in terms of raising operators acting on the ground state. Calculate the energy shifts due to the perturbation

$$V = 2\lambda xy$$

in the ground state, and in the degenerate first excited states, using first order perturbation theory. Can you interpret your result very simply? Solve the problem exactly, and compare it with a second order perturbation calculation.

[*Hints.* (a) Examine the symmetries of the unperturbed Hamiltonian. (b) Decompose the motion into center of mass motion and internal motion.]

References

There are many examples of the application of first-order perturbation theory in the textbook literature, and the references listed at the end of this book may serve as a source of further examples. For a discussion of the exact calculation of the Stark effect see

S. Borowitz, *Fundamentals of Quantum Mechanics*, W. A. Benjamin, Inc., 1967.

generating function (13.10) for the Hermite polynomials. The earlier discussion (Sec. 13) shows that the states most likely to be excited are those that have a classical amplitude of oscillation that is of the order of the displacement a; this is in agreement with the corresponding classical result. Equation (35.32) can then be used to show that the sudden approximation is valid in this case if the time required to move the equilibrium point is small in comparison with $1/n_0$ times the classical-oscillator period, where n_0 is the quantum number of the state most likely to be excited.

PROBLEMS

1. A one-dimensional harmonic oscillator of charge e is perturbed by an electric field of strength E in the positive x direction. Calculate the change in each energy level to second order in the perturbation, and calculate the induced electric dipole moment. Show that this problem can be solved exactly, and compare the result with the perturbation approximation. Repeat the calculation for a three-dimensional isotropic oscillator. Show that, if the polarizability α of the oscillator is defined as the ratio of the induced electric dipole moment to E, the change in energy is exactly $-\frac{1}{2}\alpha\mathsf{E}^2$.

2. A one-dimensional harmonic oscillator is perturbed by an extra potential energy bx^3. Calculate the change in each energy level to second order in the perturbation.

3. Find the first-order Stark effect for a hydrogen atom in the state $n = 3$. Sketch the arrangement of the levels and state the quantum numbers associated with each.

4. A system that has three unperturbed states can be represented by the perturbed hamiltonian matrix

$$\begin{bmatrix} E_1 & 0 & a \\ 0 & E_1 & b \\ a^* & b^* & E_2 \end{bmatrix}$$

where $E_2 > E_1$. The quantities a and b are to be regarded as perturbations that are of the same order and are small compared with $E_2 - E_1$. Use the second-order nondegenerate perturbation theory to calculate the perturbed eigenvalues (is this procedure correct?). Then diagonalize the matrix to find the exact eigenvalues. Finally, use the second-order degenerate perturbation theory. Compare the three results obtained.

5. A trial function ψ differs from an eigenfunction u_E by a small amount, so that $\psi = u_E + \epsilon\psi_1$, where u_E and ψ_1 are normalized and $\epsilon \ll 1$. Show that $\langle H \rangle$ differs from E only by a term of order ϵ^2, and find this term.

6. If the first $n - 1$ eigenfunctions of a particular hamiltonian are known, write a formal expression for a variation-method trial function that could be used to get an upper limit on the nth energy level.

7. Find the next terms (of order R^{-4}) in the expansion of Eq. (32.12). Show that their diagonal matrix element for the unperturbed ground state vanishes, so that there is no inverse fourth-power contribution to the van der Waals interaction.

8. Use the first nonvanishing term in the series (32.13) to get a lower limit for $-W(R)$. Compare with that obtained from the variation calculation.

is in fact $n+\frac{1}{2}$ and hence the usual quantization rule, Eq. (16.2.32). If, however, ψ actually vanishes at x_1 and x_2 because the potential barrier there is infinite (as in the case of a particle in a box), Eq. (16.2.40) [and not Eq. (16.3.32)] is relevant.‡ One can also consider an intermediate case where the barrier is infinite at one turning point and not at the other. In this case the quantization rule has an $(n+3/4)$ factor in it.

The WKB method may also be applied in three dimensions to solve the radial equation in a rotationally invariant problem. In the $l=0$ state, there is no centrifugal barrier, and the WKB wave function has the form

$$U(r) \sim \frac{1}{[p(r)]^{1/2}} \sin\left[\frac{1}{\hbar}\int_0^r p(r')\,dr'\right], \qquad p=\{2m[E-V(r)]\}^{1/2} \qquad (16.2.41)$$

where the lower limit in the phase integral is chosen to be 0, so that $U(0)=0$. The quantization condition, bearing in mind that the barrier at $r=0$ is infinite, is

$$\int_0^{r_{max}} p(r)\,dr = \left(n+\frac{3}{4}\right)\hbar\pi, \qquad n=0, 1, 2, \ldots \qquad (16.2.42)$$

where $r_{\max}$ is the turning point. This formula is valid only if $V(r)$ is regular at the origin. If it blows up there, the constant we add to n is not 3/4 but something else. Also if $l \neq 0$, the centrifugal barrier will alter the behavior near $r=0$ and change both the wave function and this constant.

*Exercise 16.2.5.** In 1974 two new particles called the ψ and ψ' were discovered, with rest energies 3.1 and 3.7 GeV, respectively (1 GeV $=10^9$ eV). These are believed to be nonrelativistic bound states of a "charmed" quark of mass $m=1.5$ GeV$/c^2$ (i.e., $mc^2=1.5$ GeV) and an antiquark of the same mass, in a linear potential $V(r)=V_0+kr$. By assuming that these are the $n=0$ and $n=1$ bound states of zero orbital angular momentum, calculate V_0 using the WKB formula. What do you predict for the rest mass of ψ'', the $n=2$ state? (The measured value is $\simeq 4.2$ GeV$/c^2$.) [Hints: (1) Work with GeV instead of eV. (2) There is no need to determine k explicitly.]

Exercise 16.2.6. Obtain Eq. (16.2.39) for the λx^4 potential by the scaling trick.

*Exercise 16.2.7** Find the allowed levels of the harmonic oscillator by the WKB method.

Exercise 16.2.8. Consider the $l=0$ radial equation for the Coulomb problem. Since $V(r)$ is singular at the turning point $r=0$, we can't use $(n+3/4)$.

(1) Will the additive constant be more or less than 3/4?

(2) By analyzing the exact equation near $r=0$, it can be shown that the constant equals 1. Using this constant show that the WKB energy levels agree with the exact results.

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‡The assumption that $V(x)$ may be linearized near the turning point breaks down and this invalidates Eq. (16.2.29).