Chapter 8
Approximate Solutions to Quantum Problems

The previous chapters may have left the (erroneous) impression that there is always an exact (and elegant) mathematical solution for every problem in quantum mechanics. In most cases there is not. One must resort to makeshift approximations, numerical solutions or combinations of both. In this chapter we discuss approximate methods that are frequently applied: perturbation theory, variational procedure, approximate matrix diagonalization, Hartree–Fock and random phase approximations. They are illustrated by means of applications to two-electron atoms, molecules, periodic potentials, etc.

8.1 Perturbation Theory

The procedure is similar to the one used in celestial mechanics, where the trajectory of a comet is first calculated by taking into account only the attraction of the sun. The (smaller) effect of planets is included in successive orders of approximation.

We divide the Hamiltonian $\hat{H}$, which we do not know how to solve exactly, into two terms. The first term, $\hat{H}_0$, is the Hamiltonian of a problem whose solution we know and which is reasonably close to the original problem; the second term, $\hat{V}$, is called the perturbation. Thus

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}, \tag{8.1}$$

$$\hat{H}_0 \varphi_n^{(0)} = E_n^{(0)} \varphi_n^{(0)}. \tag{8.2}$$

The perturbation term has been multiplied by a constant λ that is supposed to be a number less than 1. The constant λ is helpful for keeping track of the order of magnitude of the different terms of the expansion that underlies the theory. Otherwise it has no physical meaning. It is replaced by 1 in the final expressions. We solve the eigenvalue equation

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$$\hat{H}\Psi_n = E_n\Psi_n \tag{8.3}$$

by expanding the eigenvalues and the eigenstates in powers of λ and successively considering all terms corresponding to the same power of λ in (8.3):

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots , \\ \Psi_n &= \varphi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \cdots . \end{aligned} \tag{8.4}$$

The terms independent of λ yield (8.2). The terms proportional to λ give rise to the equation

$$\left(\hat{H}_0 - E_n^{(0)}\right)\Psi_n^{(1)} = \left(-\hat{V} + E_n^{(1)}\right)\varphi_n^{(0)}. \tag{8.5}$$

First, we take the scalar product of $\varphi_n^{(0)}$ with the states on each side of (8.5). The left-hand side vanishes because of (8.2). We thus obtain the first-order correction to the energy

$$E_n^{(1)} = \langle\varphi_n^{(0)}|V|\varphi_n^{(0)}\rangle. \tag{8.6}$$

Therefore, the leading order term correcting the unperturbed energy is the expectation value of the perturbation.

Next, we take the scalar product with $\varphi_p^{(0)}$ $(p \neq n)$, so that

$$\left(E_p^{(0)} - E_n^{(0)}\right)\langle\varphi_p^{(0)}|\Psi_n^{(1)}\rangle = -\langle\varphi_p^{(0)}|V|\varphi_n^{(0)}\rangle. \tag{8.7}$$

Using the states $\varphi_p^{(0)}$ as basis states, we expand

$$\Psi_n^{(1)} = \sum_{p\neq n} c_p^{(1)}\varphi_p^{(0)}, \qquad c_p^{(1)} = \frac{\langle\varphi_p^{(0)}|V|\varphi_n^{(0)}\rangle}{E_n^{(0)} - E_p^{(0)}}. \tag{8.8}$$

The still missing amplitude $c_n^{(1)}$ is determined from the normalization condition: since both Ψ_n and $\varphi_n^{(0)}$ are supposed to be normalized to unity, the terms linear in λ are

$$0 = \langle\Psi_n|\Psi_n\rangle - \langle\varphi_n^{(0)}|\varphi_n^{(0)}\rangle = \lambda\left[\langle\Psi_n^{(1)}|\varphi_n^{(0)}\rangle + \langle\varphi_n^{(0)}|\Psi_n^{(1)}\rangle\right] = 2\lambda\,\mathrm{Re}\,(c_n^{(1)}). \tag{8.9}$$

Therefore, the first-order coefficient $c_n^{(1)}$ disappears, since we can make it real by changing the (arbitrary) phase of $\varphi_n^{(0)}$.

Equations (8.6) and (8.8) determine the first-order changes in the energies and state vectors in terms of matrix elements of the perturbation with respect to the basis of zero-order states. The convergence of perturbation theory requires that $|c_p^{(1)}|^2 \ll 1$, i.e. the matrix element of the perturbation between two states should be smaller than the unperturbed distance between these states. In particular, perturbation theory cannot be applied if there are non-vanishing matrix elements

between degenerate states. In these cases, we must resort to either variational (Sect. 8.2) or diagonalization procedures (Sect. 8.5).

The second-order correction to the energy is given by

$$E_n^{(2)} = \sum_{p \neq n} \frac{|\langle \varphi_p^{(0)} | V | \varphi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_p^{(0)}}. \tag{8.10}$$

This perturbation theory is called the Raleigh–Schrödinger perturbation theory. Its apparent simplicity disappears in higher orders of perturbation, due to the increase in the number of contributing terms. A formal simplification may be achieved by summing up partial series of terms. For instance, in the Brillouin–Wigner perturbation theory, one replaces the unperturbed energy $E_n^{(0)}$ of the state n by the exact energy E_n in the denominators. For the case of the energy expansion, one obtains

$$\begin{aligned} E_n &= E_n^{(0)} + \langle \varphi_n^{(0)} | V | \varphi_n^{(0)} \rangle + \sum_{p \neq n} \frac{|\langle \varphi_p^{(0)} | V | \varphi_n^{(0)} \rangle|^2}{E_n - E_p^{(0)}} + \cdots \\ &= E_n^{(0)} + \langle \varphi_n^{(0)} | V | \varphi_n^{(0)} \rangle + \sum_{p \neq n} \frac{|\langle \varphi_p^{(0)} | V | \varphi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_p^{(0)}} \\ &\quad - \sum_{p \neq n} \frac{|\langle \varphi_p^{(0)} | V | \varphi_n^{(0)} \rangle|^2 \langle \varphi_n^{(0)} | V | \varphi_n^{(0)} \rangle}{\left(E_n^{(0)} - E_p^{(0)}\right)^2} + \cdots . \end{aligned} \tag{8.11}$$

The last term appears as a third-order term in the Raleigh–Schrödinger perturbation theory. It does not exist[1] in the Brillouin–Wigner expansion, since it has been taken into account through the replacement in the denominator of the second-order term (8.10). However, the advantage of reducing the number of terms may be compensated by a decrease in the convergence of the perturbation expansion, associated with the nature of the partial summations. Moreover, different powers of λ may be present in many terms of the Brillouin–Wigner series.

There is an elegant and useful formulation of perturbation theory conceived by Feynman. This uses diagrams carrying both a precise mathematical meaning and a description of the processes involved [59]. The "finest hour" of perturbation theory is represented by the calculation of the gyromagnetic electron value to nine significant figures, using quantum electrodynamics (see Sect. 5.2.2).

The ground state energy of the He atom is calculated using perturbation theory in Sect. 8.3.

[1] One can prove that the Brillouin–Wigner expansion does not contain terms in which the state $\varphi_n^{(0)}$ appears in the numerator as an intermediate state.

8.2 Variational Procedure

This approximation may be considered as the inverse of the perturbation procedure: instead of working with a fixed set of unperturbed states, one guesses a trial state Ψ, which may be expanded in terms of the basis set of eigenstates φ_E of the Hamiltonian ($\Psi = \sum_E c_E \varphi_E$):

$$\langle \Psi | H | \Psi \rangle = \sum_E E |c_E|^2 \geq E_0 \sum_E |c_E|^2 = E_0, \tag{8.12}$$

where E_0 is the ground state energy. The state Ψ may depend on some parameter, and the expectation value of the Hamiltonian is minimized with respect to this parameter. One thus obtains an upper limit for the ground state energy of the system.

The fact that the energy is an extremum guarantees that if the trial wave function is wrong by something of the order of δ, the variational estimate of the energy is off by something of the order δ^2. So one can be rewarded with a good energy estimate, even though the initial wave function may be only a fair guess.

The ground state energy obtained in first-order perturbation theory $E_0^{(0)} + \langle \varphi_0^{(0)} | V | \varphi_0^{(0)} \rangle$ is an expectation value of the total Hamiltonian and is thus equivalent to a non-optimized variational calculation.

8.3 Ground State of the He Atom

This three-body problem may be reduced to a two-body problem by again considering a very massive nucleus. However, even the remaining problem is difficult to solve because of the presence of the Coulomb repulsion V between the two electrons. The total Hamiltonian is $\hat{H}_0 + V$, where

$$\hat{H}_0 = -\frac{\hbar^2}{2M} \left(\nabla_1^2 + \nabla_2^2 \right) - \frac{Ze^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \qquad V = \frac{e^2}{4\pi\epsilon_0 r_{12}}. \tag{8.13}$$

Here $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the electrons.

We know how to solve the problem of two electrons moving independently of each other in the Coulomb potential of the He nucleus. Because the ground state energy of a hydrogen-like atom is proportional to Z^2 and there are two electrons, the unperturbed energy is $8E_\mathrm{H}$, where E_H is the energy of the electron in the H atom. The antisymmetrized two-electron state vector of the ground state in the He atom is discussed in Sect. 7.2. Using this state, the first-order correction to the energy is (Sect. 8.7*)

$$E_{\mathrm{g.s.}}^{(1)} = \left\langle \varphi_{\mathrm{g.s.}} \left| \frac{e^2}{4\pi\epsilon_0 r_{12}} \right| \varphi_{\mathrm{g.s.}} \right\rangle = -\frac{5}{2} E_\mathrm{H}. \tag{8.14}$$

Therefore, the total energy becomes $5.50E_{\mathrm{H}}$, which constitutes an improved approximation to the experimental result $5.81E_{\mathrm{H}}$ compared with the unperturbed value $8E_{\mathrm{H}}$.

As mentioned in Sect. 8.2, one may improve the predictions for the ground state by a variational calculation. In this case we may write the expectation value of the kinetic energy, of the potential energy and the Coulomb repulsion as functions of the parameter Z^* entering the wave function. The value $Z = 2$ is kept in the Hamiltonian:

$$\langle \varphi_{\mathrm{g.s.}} | H | \varphi_{\mathrm{g.s.}} \rangle_{Z^*} = -2(Z^*)^2 E_{\mathrm{H}} + 4ZZ^* E_{\mathrm{H}} - \frac{5}{4} Z^* E_{\mathrm{H}}. \tag{8.15}$$

Minimization with respect to Z^* yields the effective value $Z^* = 1.69$ for He (instead of 2), which is an indication that the electrons mutually screen the nuclear attraction. The final result is $\langle \varphi_{\mathrm{g.s.}} | H | \varphi_{\mathrm{g.s.}} \rangle_{Z=1.69} = 5.69E_{\mathrm{H}}$, and this is in even better agreement with the experimental value than the first-order perturbation result.

To apply the variational procedure to excited states, one must ensure their orthogonality with lower energy states, for the resulting value of the minimization parameter.

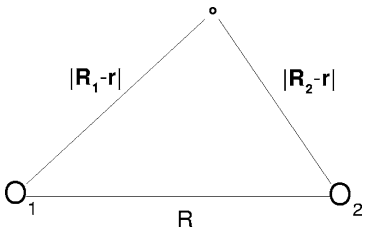
8.4 Molecules

Molecules are made up of nuclei and electrons. The theoretical description of this many-body system is facilitated by the very different masses of the two constituents, which allows us to decouple their respective motions. The procedure is called the Born–Oppenheimer approximation. In principle, it is possible to begin by solving the problem of motion of electrons subject to the (static) field of the nuclei and to the field of other electrons. In this first step, the nuclear coordinates $\boldsymbol{R}_i$ are treated as parameters. Minimization of the energy $W(\boldsymbol{R}_i)$ with respect to these parameters yields their equilibrium values. A subsequent step consists in allowing small departures of the nuclei from their equilibrium position and using the associated increase in the energy W as the restoring force for the oscillatory motion. Finally, the molecules may also perform collective rotations without changing the relative positions of the electrons and the nuclei.

8.4.1 Intrinsic Motion: Covalent Binding

We illustrate the procedure for the case of the molecular hydrogen ion $H_2{}^+$. Figure 8.1 represents the two protons 1 and 2 and the electron. The assumption that the protons are at rest simplifies the Hamiltonian to

Fig. 8.1 The hydrogen ion



$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 - \frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}-\boldsymbol{R}_1|} - \frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}-\boldsymbol{R}_2|} + \frac{e^2}{4\pi\epsilon_0 R}, \tag{8.16}$$

where $R = |\boldsymbol{R}_1 - \boldsymbol{R}_2|$. Although in this particular case, exact numerical solutions may be obtained by solving the Schrödinger equation in elliptical coordinates, it is more instructive to approximate the solution by means of a variational procedure.

If the distance R is very large, the two (degenerate) solutions describe a H atom plus a dissociated proton. The two orbital wave functions are

$$\varphi_1 = \varphi_{100}(|\boldsymbol{r}-\boldsymbol{R}_1|), \qquad \varphi_2 = \varphi_{100}(|\boldsymbol{r}-\boldsymbol{R}_2|). \tag{8.17}$$

Note that such wave functions are orthogonal only for very large values of R. In fact, their overlap is $\langle 1|2\rangle = 1$ for $R = 0$.

The requirement of antisymmetry between the two protons must be taken into account. As in Sect. 7.2, the spin of the two protons may be coupled to 1 (symmetric spin states) or to 0 (antisymmetric spin states). The corresponding spatial wave functions should thus be antisymmetric and symmetric, respectively:

$$\varphi_\mp = \frac{\varphi_1 \mp \varphi_2}{\sqrt{2(1 \mp \langle 1|2\rangle)}}. \tag{8.18}$$

The energy to be minimized with respect to the distance R is

$$\begin{aligned} E_\pm(R) &= \langle \pm|H|\pm\rangle \\ &= E_{100} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{e^2}{4\pi\epsilon_0(1 \pm \langle 1|2\rangle)}\left\langle 2\left|\frac{1}{|\boldsymbol{r}-\boldsymbol{R}_1|}\right|2\right\rangle \\ &\quad \mp \frac{e^2}{4\pi\epsilon_0(1 \pm \langle 1|2\rangle)}\left\langle 1\left|\frac{1}{|\boldsymbol{r}-\boldsymbol{R}_1|}\right|2\right\rangle, \end{aligned} \tag{8.19}$$

which has the limits

$$\lim_{R\to 0} E_\pm \to \infty, \qquad \lim_{R\to\infty} E_\pm = E_{100}. \tag{8.20}$$

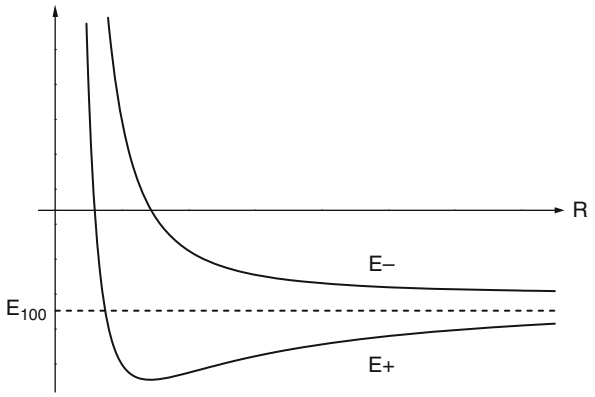


Fig. 8.2 Lowest energies of the hydrogen ion as a function of the distance between protons

Since the matrix element in the third line of (8.19) is positive, we conclude that the energy corresponding to the spatially symmetric wave function lies lowest. In fact, the two curves are plotted in Fig. 8.2. Only the energy corresponding to φ_+ displays a minimum. This may be interpreted as being due to the build-up of the electron density between the two nuclei, which allows for the screening of the Coulomb repulsion. This type of binding is called covalent binding.[2]

8.4.2 Vibrational and Rotational Motions

We consider here the somewhat more general case of a diatomic molecule with masses M_1 and M_2, respectively. First we perform the well-known separation between the relative and center of mass operators:

$$\begin{aligned} \hat{\boldsymbol{R}} &= \hat{\boldsymbol{R}}_1 - \hat{\boldsymbol{R}}_2, \qquad \hat{\boldsymbol{R}}_\mathrm{g} = \frac{M_1}{M_\mathrm{g}}\hat{\boldsymbol{R}}_1 + \frac{M_2}{M_\mathrm{g}}\hat{\boldsymbol{R}}_2, \\ \hat{\boldsymbol{P}} &= \frac{M_2}{M_\mathrm{g}}\hat{\boldsymbol{P}}_1 - \frac{M_1}{M_\mathrm{g}}\hat{\boldsymbol{P}}_2, \qquad \hat{\boldsymbol{P}}_\mathrm{g} = \hat{\boldsymbol{P}}_1 + \hat{\boldsymbol{P}}_2. \end{aligned} \tag{8.21}$$

The inversion of definitions (8.21) yields the kinetic energy

$$\frac{\hat{\boldsymbol{P}}_1^2}{2M_1} + \frac{\hat{\boldsymbol{P}}_2^2}{2M_2} = \frac{\hat{\boldsymbol{P}}_\mathrm{g}^2}{2M_\mathrm{g}} + \frac{\hat{\boldsymbol{P}}^2}{2\mu}. \tag{8.22}$$

Here $M_\mathrm{g} = M_1 + M_2$ is the total mass and $\mu \equiv M_1 M_2 / M_\mathrm{g}$ is the reduced mass.

[2] See also the example in Sect. 3.2.

If the potential energy $V(R)$ depends only on the distance between the ions, the center of mass moves as a free particle. This problem has already been discussed in Sect. 4.3. The kinetic energy associated with the relative motion may be expressed in spherical coordinates, as in (6.1), with the substitution $M \to \mu$.

Let us split the relative Hamiltonian into rotational and vibrational contributions, viz.,

$$\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_{\text{vib}},$$

$$\hat{H}_{\text{rot}} = \frac{1}{2\mu R^2}\hat{\boldsymbol{L}}^2, \tag{8.23}$$

$$\hat{H}_{\text{vib}} = -\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}R^2} + \frac{2}{R}\frac{\mathrm{d}}{\mathrm{d}R}\right) + V(R). \tag{8.24}$$

We now assume that the interactions between the ions stabilize the system at the relative distance R_0. The difference $y = R - R_0$ will be such that $|y| \ll R_0$.

Rotational Motion

The Hamiltonian for the rotational motion may be approximated as (see Fig. 8.3)

$$\hat{H}_{\text{rot}} = \frac{1}{2\mathcal{I}}\hat{L}^2, \qquad \mathcal{I} = \mu R_0^2, \tag{8.25}$$

where $\mathcal{I}$ is the moment of inertia. The eigenfunctions are labeled by the quantum numbers l, m_l (Sect. 5.1.2). The energies are obtained by replacing the operator $\hat{\boldsymbol{L}}^2$ in (8.25) by its eigenvalues $\hbar^2 l(l+1)$. The photon energy corresponding to the transition between neighboring states increases linearly with l, so that

$$\Delta(l \to l-1) = \frac{\hbar^2}{\mathcal{I}} l. \tag{8.26}$$

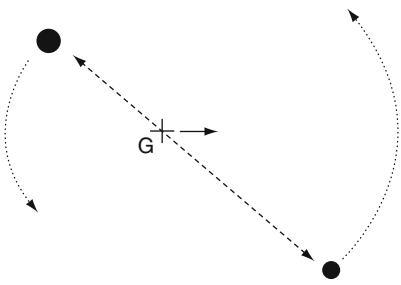


Fig. 8.3 Vibrational (*dashed line*), rotational (*dotted lines*) and translation of the center of mass G (*continuous line*) of a diatomic molecule

Vibrational Motion

If the stabilization at $R \approx R_0$ is sufficiently good we may extend the domain of the radial coordinate from 0 to $-\infty$, since the wave function should be increasingly small for negative values of R. Simultaneously, the R^2 factor in the volume element may be eliminated from the integrals by the substitution $\Psi(R) \to \Phi(R)/R$. In such a case the radial Schrödinger equation transforms into a linear equation of the type seen in Chap. 4:

$$-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2}{\mathrm{d}R^2}+\frac{2}{R}\frac{\mathrm{d}}{\mathrm{d}R}\right)\Psi + V(R)\Psi = E\Psi \longrightarrow -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2}\Phi + V(R)\Phi = E\Phi, \tag{8.27}$$

with the boundary conditions $\Phi(\pm\infty) = 0$.

Finally, the Taylor expansion of the potential around the equilibrium position R_0 and the replacement of the coordinate R by $y = R - R_0$ yield the harmonic oscillator Hamiltonian discussed in Sects. 3.3 and 4.2 (see Fig. 8.3)

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}y^2}+\frac{1}{2}\left.\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right|_{R=R_0} y^2\right]\Phi = \big[E - V(R_0)\big]\Phi. \tag{8.28}$$

The vibrational states are equidistant from each other (Fig. 3.2). The photon spectrum displays the single frequency

$$\Delta(N \to N-1) = \hbar\omega = \hbar\sqrt{\frac{1}{\mu}\left.\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right|_{R=R_0}}. \tag{8.29}$$

8.4.3 Characteristic Energies

The diatomic molecule is the simplest illustration of a general feature: the breaking of the spherical symmetry produced by the shape of the intrinsic system generates rotational degrees of freedom; if the amount of this breaking is measured by a minimization parameter (the distance R_0), there appear vibrational degrees of freedom around this value.

The intrinsic motion of electrons and the vibrational and rotational motion of nuclei are associated with different characteristic energies. The order of magnitude for intrinsic transitions should be similar to the excitation energies in atoms

$$E_{\mathrm{intr}} \approx -E_H = \frac{\hbar^2}{2a_0^2 M}, \tag{8.30}$$

since the same Coulomb interaction and similar interparticle distances are present. Here a_0 is the Bohr radius (Table 6.1). The potential energy of the vibrational motion

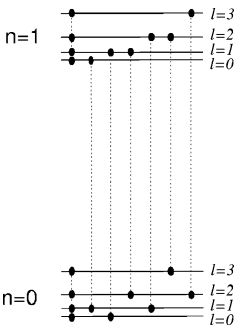


Fig. 8.4 Vibrational and rotational excitations of a molecule. *Dotted lines* represent allowed transitions, according to the definition (9.71)

originates also in the Coulomb potential and thus should be of the same order of magnitude as E_{intr}

$$E_{\text{vib}} = \hbar\sqrt{\frac{E_{\text{intr}}}{2a_0^2\mu}} \approx \frac{\hbar^2}{a_0^2\sqrt{2M\mu}} \approx \sqrt{\frac{M}{M_p}}\,E_{\text{intr}} \tag{8.31}$$

Rotational energies are given by (8.26)

$$E_{\text{rot}} \approx \frac{\hbar^2}{2a_0^2\mu} \approx \frac{M}{M_p}\,E_{\text{intr}}. \tag{8.32}$$

Since the ratio between the electron and the proton masses $M/M_{\text{p}} \approx 1/2{,}000$ (see Table A.1), the transitions between vibrational states occupy an intermediate energy range compared to those corresponding to intrinsic electron transitions or to transitions between rotational states. Therefore, the molecular spectrum displays vibrational states on top of each intrinsic excitation and rotational states on top of each vibrational state (see Fig. 8.4). The electromagnetic radiation associated with transitions between intrinsic, vibrational and rotational states appears, successively, in the visible, infrared and radiofrequency regions of the optical spectrum.

As the energies of the rotational and vibrational excitations increase, the approximations become less reliable:

- Terms that are functions of y will appear in the rotational Hamiltonian, coupling the rotational and vibrational motion
- Higher order terms in the Taylor expansion of the potential become relevant

8.5 Approximate Matrix Diagonalizations

If the conditions for applying perturbation theory are not satisfied, we may resort to a diagonalization procedure. This is obviously necessary if there are degenerate or close-lying states. This is the case if two or more particles are added to a closed shell,

whether it be atomic or nuclear. The size of the matrix to be diagonalized may be reduced due to physical considerations, for example, when we use the symmetries of the Hamiltonian. If we are only interested in the ground state and neighboring states, we may also simplify the problem by taking into account only those states which are close in energy to the ground state.

It is also possible to include those contributions to the matrix elements of the Hamiltonian to be diagonalized that arise from states not included in the diagonalization. One may use either the technique of folded diagrams (a generalization of Raleigh–Schrödinger perturbation theory) [61] or the Bloch–Horowitz procedure (an extension of the Brillouin–Wigner expansion) [62].

An alternative procedure consists in simplifying the expressions for the matrix elements. This includes eliminating many of them (see Problem 12). In such cases, good insight is required to avoid distorting the physical problem.

8.5.1† Approximate Treatment of Periodic Potentials

This example illustrates the interplay between exact diagonalization and perturbation theory that can be applied in more complicated situations. We treat the same problem as in Sect. 4.6†, but in the limit of a small periodic potential $V(x)$.

We choose the free-particle Hamiltonian $H_0 = \frac{1}{2M}\hat{p}^2$ as zero-order Hamiltonian. The unperturbed energies are given in Fig. 8.5a, as a function of the wave number k. If $V(x) = V(x + d)$, a Fourier transform of the potential yields

$$V(x) = \sum_n V_n, \qquad V_n = v_n \exp\left(\frac{i2\pi nx}{d}\right), \quad n = 0, \pm 1, \pm 2, \ldots \tag{8.33}$$

Therefore, the non-vanishing matrix elements of the perturbation are

$$\langle k'|V_n|k\rangle = v_n, \qquad \text{if } k' - k = \frac{2\pi n}{d}, \tag{8.34}$$

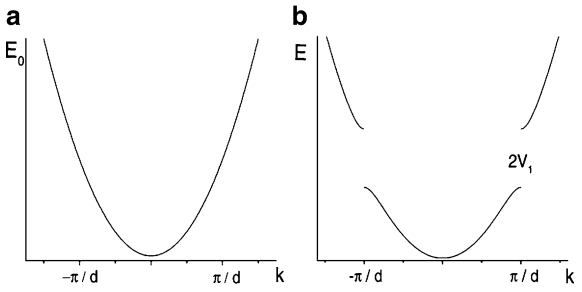


Fig. 8.5 Bands in periodic potentials. The unperturbed parabolic energies are given as functions of k in (**a**). The eigenvalue E_- is plotted in the interval $0 \le |k| \le \frac{\pi}{d}$ and E_+ for $\frac{\pi}{d} \le |k|$ in (**b**)

and the Hamiltonian matrix is of the form[3]

$$\begin{pmatrix} \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \frac{\hbar^2}{2M}\left(k-\frac{4\pi}{d}\right)^2 & v_1 & v_2 & v_3 & \cdots \\ \cdots & v_1 & \frac{\hbar^2}{2M}\left(k-\frac{2\pi}{d}\right)^2 & v_1 & v_2 & \cdots \\ \cdots & v_2 & v_1 & \frac{\hbar^2}{2M}k^2 & v_1 & \cdots \\ \cdots & v_3 & v_2 & v_1 & \frac{\hbar^2}{2M}\left(k+\frac{2\pi}{d}\right)^2 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}. \tag{8.35}$$

We concentrate on the non-diagonal terms v_1. However small, they cannot be treated in perturbation theory, because they connect degenerate states: the state with $k = \frac{\pi}{d}$ has the same unperturbed energy as the state with $k' = k - \frac{2\pi}{d} = -\frac{\pi}{d}$. Thus, we must first proceed to make a diagonalization between degenerate (or quasi-degenerate) states, i.e. we must put to zero the determinant

$$\begin{vmatrix} \frac{\hbar^2}{2M}\left(k-\frac{2\pi}{d}\right)^2 - E & v_1 \\ v_1 & \frac{\hbar^2}{2M}k^2 - E \end{vmatrix} = 0. \tag{8.36}$$

The eigenvalues

$$E_\pm = \frac{\hbar^2}{2M}\left(k^2 - k\frac{2\pi}{d} + \frac{2\pi^2}{d^2} \pm \sqrt{\frac{4\pi^2}{d^2}\left(k-\frac{\pi}{d}\right)^2 + \left(\frac{2Mv_1}{\hbar^2}\right)^2}\right) \tag{8.37}$$

are plotted as functions of k in Fig. 8.5b. There are no states in the interval $\frac{1}{2M}\left(\frac{\hbar\pi}{d}\right)^2 - v_1 \le E \le \frac{1}{2M}\left(\frac{\hbar\pi}{d}\right)^2 + v_1$. A gap of size $2v_1$ appears in the spectrum, pointing to the existence of two separate bands.

In the region $|k| \approx \frac{\pi}{d}$, the remaining non-diagonal terms v_n may be treated as perturbations, if they are sufficiently small. Unfortunately, they usually are not so in realistic cases.

8.6 Independent-Particle Approximations

8.6.1† The Hartree–Fock Approximation

On several occasions we have used with good results a product of single-particle states to represent the ground state of many-fermion problems (atoms, nuclei, metals, etc.)

[3] We disregard v_0 since it only affects the zero-point energy.

$$\varphi_0 = \prod_h a_h^+ \,|\text{vacuum}\rangle, \tag{8.38}$$

where h denotes occupied states. Of course this can only be an approximation if the Hamiltonian includes n-body interactions, with $n > 1$. The Hartree–Fock procedure determines the best single particle set to be used in such cases. It consists on the replacement of some (large) one-body operators by their expectation values, thus neglecting their fluctuations.

Let us consider a system of identical fermions within the formalism of second quantization. The Hamiltonian is

$$\hat{H} = \sum_{kj} \langle k|H_1|j\rangle c_k^+ c_j + \frac{1}{2}\sum_{kljm} \langle kl|H_2|jm\rangle c_k^+ c_l^+ c_m c_j, \tag{8.39}$$

where $\hat{H}_\nu$ contains ν-body terms (ν=1,2). States (8.38) are eigenstates of an independent particle Hamiltonian

$$\hat{H}_{\text{HF}} = \sum_i \epsilon_i \, a_i^+ a_i. \tag{8.40}$$

The two sets of single-fermion creation operators are related through a transformation

$$a_i^+ = \sum_j \lambda_{ij} \, c_j^+. \tag{8.41}$$

To find the Hartree–Fock single-particle energies ϵ_i and the amplitudes λ_{ij}, we calculate the commutators

$$[\hat{H}_{HF}, a_i^+] = \sum_k \epsilon_i \lambda_{ik} c_k^+ \tag{8.42}$$

$$\begin{aligned}
[\hat{H}, a_i^+] &= \sum_q \lambda_{iq} \left[\sum_k \langle k|H_1|q\rangle c_k^+ + \frac{1}{2}\sum_{klj} (\langle kl|H_2|qj\rangle - \langle kl|H_2|jq\rangle) c_k^+ c_l^+ c_j \right] \\
&= \sum_{qk} \lambda_{iq} c_k^+ \left[\langle k|H_1|q\rangle + \sum_{lj} (\langle kl|H_2|qj\rangle - \langle kl|H_2|jq\rangle) c_l^+ c_j \right] \\
&\approx \sum_{qk} \lambda_{iq} c_k^+ \left[\langle k|H_1|q\rangle + \sum_h (\langle kh|H_2|qh\rangle - \langle kh|H_2|hq\rangle) \right].
\end{aligned} \tag{8.43}$$

In deriving the last line, we have replaced the operator $c_l^+ c_j \to \delta_{lj}$ if $l = j = h$ (h = occupied state). Equating the coefficients of c_k^+ from (8.42) and (8.43) yields the eigenvalue matrix equations (3.11)

$$\epsilon_i \, \lambda_{ik} = \sum_q \left[\langle k|H_1|q\rangle + \sum_h (\langle kh|H_2|qh\rangle - \langle kh|H_2|hq\rangle) \right] \lambda_{iq}, \qquad (8.44)$$

which we know how to solve to obtain energies and amplitudes.

However, the replacement of $c_l^+ c_j$ by δ_{lj} would be a good approximation for the number operator acting on the ground state (8.38), only if the set c_j^+ of creation operators is the same as the set a_i^+ appearing in (8.38). In general, this is not the case, since the initial guess may be arbitrary, aside from some boundary conditions [see, for instance (7.13)]. We iterate the previous process, starting now from the new set a_i defined by the transformation (8.41) with the amplitudes λ_{ik} just obtained from (8.44), until convergence to a unique set is obtained.

The matrix elements of $\hat{H}_2$ in (8.44) can be interpreted as due to the one-body potential produced by all the particles in occupied states. The second contribution of $\hat{H}_2$ is due to the antisymmetry of the fermion state (8.38) and is called the exchange term. The Hartree approximation is obtained by neglecting this last contribution.

The lowest excited states $\varphi_{ph} = a_p^+ a_h \varphi_0$ are obtained by promoting a particle from an occupied state h to an empty state p. Their excitation energy is given by the difference $\epsilon_p - \epsilon_h$. The matrix elements between the ground and particle-hole states vanish

$$\langle ph|H|0\rangle = 0. \qquad (8.45)$$

8.6.2† *The Random–Phase Approximation (RPA)*

Products of fermion operators may act as bosons. In particular, the commutation of the products

$$\gamma_{ph}^+ \equiv a_p^+ a_h, \qquad (8.46)$$

used in the last paragraph of the Hartree–Fock subsection, is

$$\begin{aligned} [a_h^+ a_p, a_{p'}^+ a_{h'}] &= \delta_{p'p} \, a_h^+ a_{h'} - \delta_{h'h} \, a_{p'}^+ a_p \approx \delta_{p'p} \, \delta_{h'h} \\ [a_p^+ a_h, a_{p'}^+ a_{h'}] &= [a_h^+ a_p, a_{h'}^+ a_{p'}] = 0, \end{aligned} \qquad (8.47)$$

where we have used the same approximation $a_h^+ a_{h'} \approx \delta_{h'h}$ involved in the Hartree–Fock case. Therefore, the set of operators $\gamma_{ph}^+, \gamma_{ph}$ obey boson commutation relations (within the approximation).

The Hamiltonian (8.40) may be written as

$$\hat{H}_{\rm HF} \approx \sum_{ph} e_{ph} \gamma_{ph}^+ \gamma_{ph}, \qquad e_{ph} = \epsilon_p - \epsilon_h, \qquad (8.48)$$

as can be verified by commuting both sides with γ_{ph}^+ or with γ_{ph}.

In addition to the terms in the Hamiltonian determining $\hat{H}_{\rm HF}$, there are residual contributions of $\hat{H}$. Some of them may be expressed in terms of the bosons (8.46) and thus, they represent (quadratic) boson interactions:

$$\hat{H}_{2b} = \frac{1}{2} \sum_{(ph),(p'h')} \left(\langle ph'|H_2|hp'\rangle \gamma^+_{ph}\gamma_{p'h'} + \langle pp'|H_2|hh'\rangle \gamma^+_{ph}\gamma^+_{p'h'} \right) + \text{h.c.} \tag{8.49}$$

The objective now is to obtain a set of uncoupled bosons, giving rise to the Hamiltonian

$$\hat{H}_b \equiv \sum_n \hbar\omega_n \Gamma^+_n \Gamma_n = \hat{H}_{\rm HF} + \hat{H}_{2b}. \tag{8.50}$$

The procedure is similar to that used in the Hartree–Fock case. One starts by defining the boson transformation [which plays a similar role to (8.41)]

$$\Gamma^+_n = \lambda_{n,(ph)}\gamma^+_{ph} - \mu_{n,(ph)}\gamma_{ph}. \tag{8.51}$$

Subsequently, we equate the terms proportional to γ^+_{ph} and to γ_{ph} in the commutation of both sides of (8.50) with the uncoupled bosons Γ^+_n. One obtains a set of 2ν linear equations, ν being the number of possible pairs (ph)

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} \lambda_n \\ \mu_n \end{pmatrix} = \omega_n \begin{pmatrix} \lambda_n \\ \mu_n \end{pmatrix}, \tag{8.52}$$

where

$$\begin{aligned} \langle p'h'|A|ph\rangle &= e_{ph}\delta_{p'p}\delta_{h'h} + \langle p'h|H_2|h'p\rangle \\ \langle p'h'|B|ph\rangle &= \langle p'p|H_2|h'h\rangle. \end{aligned} \tag{8.53}$$

The solution is symmetrical between positive and negative values of ω_n and an interchange between λ_n and μ^*_n. Only the positive energies are considered

It is usually convenient to further limit the possible pairs (ph) by requiring, for instance, that the bosons carry a definite momentum or angular momentum, parity, etc.

Although the RPA modes constitute simple boson excitations, they have a complicated (collective) structure from the point of view of the original constituents of the system (electrons, ions, nuclei, etc.). They may occupy regions of the spectrum that cannot be simply covered by particle-hole excitations (8.48). See, for instance, Sects. 7.4.4†, 8.4.2 and 10.1.6†.

The RPA excitation spectrum replaces the HF particle-hole spectrum. It is expected to be more accurate, since it takes into account residual interactions (8.49) not included in (8.48). However, if many bosons γ^+_{ph} (8.46) become admixed in the ground state through the RPA correlations, the approximation (8.47) becomes

less valid. Corrections to the Hartree approximation + RPA lie beyond the scope of this text.

8.7* Matrix Elements Involving the Inverse of the Interparticle Distance

Although the integrals involved may be found in tables, we calculate them explicitly as a quantum mechanical exercise. The inverse of the distance between two particles may be expanded as

$$\frac{1}{r_{12}} = \frac{1}{r_2} \sum_l \left(\frac{r_1}{r_2} \right)^l P_l(\cos \alpha_{12}), \qquad r_1 < r_2. \tag{8.54}$$

Here P_l is the Legendre polynomial of order l (Sect. 5.5*), a function of the angle α_{12} subtended by the two vectors $\boldsymbol{r}_1, \boldsymbol{r}_2$. It may be expressed by coupling two spherical harmonics to zero angular momentum (5.66).

Next, we evaluate matrix elements such as

$$\begin{aligned}
&\left\langle n_1 l_1 m_1 n_2 l_2 m_2 \left| \frac{1}{r_{12}} \right| n_1 l_1 m_1 n_2 l_2 m_2 \right\rangle \\
&\quad = N_{n_1 l_1}^2 N_{n_2 l_2}^2 \int_0^\infty |R_{n_1 l_1}(1)|^2 r_1^2 \mathrm{d}r_1 \int_0^\infty |R_{n_2 l_2}(2)|^2 r_2^2 \mathrm{d}r_2 \\
&\qquad \times \int_0^{4\pi} |Y_{l_1 m_1}(1)|^2 \mathrm{d}\Omega_1 \int_0^{4\pi} |Y_{l_2 m_2}(2)|^2 \mathrm{d}\Omega_2 / r_{12} \\
&\quad = N_{n_1 l_1}^2 N_{n_2 l_2}^2 \sum_l \frac{4\pi}{2l+1} \int_0^\infty |R_{n_1 l_1}(1)|^2 r_1^2 \mathrm{d}r_1 \\
&\qquad \times \left[\frac{1}{r_1^{l+1}} \int_0^{r_1} |R_{n_2 l_2}(2)|^2 r_2^{l+2} \mathrm{d}r_2 + r_1^l \int_{r_1}^\infty |R_{n_2 l_2}(2)|^2 r_2^{1-l} \mathrm{d}r_2 \right] \\
&\qquad \times \sum_{m_l=-l}^{m_l=l} (-1)^{l-m_l} \langle Y_{l_1 m_1} | Y_{l m_l} | Y_{l_1 m_1} \rangle \langle Y_{l_2 m_2} | Y_{l(-m_l)} | Y_{l_2 m_2} \rangle .
\end{aligned} \tag{8.55}$$

The angular integrals restrict the values of l in the summation (see Problem 5 in Chap. 5). If at least one of the particles is in an s state, only one l term survives. If both particles are in s states,

$$\left\langle n_1 00 n_2 l_2 m_2 \left| \frac{1}{r_{12}} \right| n_1 00 n_2 l_2 m_2 \right\rangle = N_{n_1 0}^2 N_{n_2 l_2}^2 \int_0^\infty |R_{n_1 0}(1)|^2 r_1^2 \mathrm{d}r_1 \times \left[\frac{1}{r_1} \int_0^{r_1} |R_{n_2 l_2}(2)|^2 r_2^2 \mathrm{d}r_2 + \int_{r_1}^\infty |R_{n_2 l_2}(2)|^2 r_2 \mathrm{d}r_2 \right], \tag{8.56}$$

which yields the value (8.14) for $n_1 = n_2 = 1$.

Problems

Problem 1. 1. Obtain the expression for the second-order correction to the energy in perturbation theory and show that this correction is always negative for the ground state.
2. Calculate the second-order correction to the eigenstate.

Problem 2. Assume that the zero-order Hamiltonian and the perturbation are given by the matrices

$$\hat{H}_0 = \begin{pmatrix} 5 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \qquad \hat{V} = \begin{pmatrix} 0 & c & 0 \\ c & 0 & 0 \\ 0 & 0 & 2c \end{pmatrix}.$$

1. Calculate the first-order perturbation corrections to the energies.
2. Calculate the second-order perturbation corrections to the energies.
3. Obtain the first-order corrections to the vector states.
4. Obtain the second-order corrections to the vector states.
5. Expand the exact energies in powers of c and compare the results with those obtained in perturbation theory:

$$(1+x)^{1/2} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \frac{1}{16}x^3 - \cdots .$$

Problem 3. 1. Calculate the first- and second-order corrections to the ground state energy of a linear harmonic oscillator if a perturbation $V(x) = kx$ is added, and compare with the exact value.
2. Do the same if the perturbation is $V(x) = bx^2/2$.

Problem 4. 1. Calculate the lowest relativistic correction to the ground state energy of a linear harmonic oscillator. Hint: expand the relativistic energy $\sqrt{M^2c^4 + c^2p^2}$ in powers of p/Mc.
2. Obtain the order of magnitude of the ratio between the relativistic correction and the non-relativistic value in the molecular case.

Problem 5. Obtain the vector state up to second order in the Brillouin–Wigner perturbation theory. Compare with the results (8.8) and Problem 1.

Problem 6. Show that the Brillouin–Wigner perturbation theory already yields the exact results (3.19) in second order, for a Hamiltonian of the form (3.18). Hint: use

$$E_a = \langle a|H|a\rangle + \frac{|\langle a|H|b\rangle|^2}{E_a - \langle b|H|b\rangle}.$$

Problem 7. Minimize the ground state energy by taking the mass as the variation in the lowest harmonic oscillator state and using the harmonic oscillator potential plus the relativistic kinetic energy as Hamiltonian. Include as many powers of p^2/M^2c^2 in the latter as are necessary to obtain an improvement over the perturbation results of Problem 5:

1. Write the expectation value of the Hamiltonian as a function of M^*/M.
2. Write the minimization condition.
3. Solve this equation in powers of $\hbar\omega/Mc^2$.
4. Expand the energies in powers of $\hbar\omega/Mc^2$.

Problem 8. Calculate the perturbation correction for the two $1s2p$ electron states in the He atom. Explain why perturbation theory may be used in spite of the existing degeneracies.

Problem 9.
1. In units of E_{H}, calculate the first-order perturbation correction for the ground state energy of the He atom, the ionized Li atom and the doubly ionized Be atom.
2. Obtain the variational energies using the effective number of electrons Z^* as the variational parameter.
3. Compare with the experimental values: -79 eV (He), -197 eV (Li^+), -370 eV (Be^{++}).

Problem 10. Substitute $R \to R_0 + y$ in the rotational Hamiltonian (8.23) and expand the Hamiltonian in powers of y up to quadratic order. Calculate the correction for the energy in perturbation theory, using the product of the rotational and vibrational bases as an unperturbed basis

$$(1+a)^{-2} = 1 - 2a + 3a^2 + \cdots .$$

Problem 11. Two He atoms are attracted by a Van der Waals potential $V(R) = 4\epsilon\left[\left(\frac{\sigma}{\kappa}\right)^1 2 - \left(\frac{\sigma}{\kappa}\right)^6\right]$, with $\epsilon = 8.75 \times 10^{-4}$ eV and $\sigma = 2.56$ Å. Find

1. The energy ϵ_0 and separation distance R_0 at equilibrium.
2. The characteristic vibrational energy $\hbar\omega$.
3. The characteristic rotational energy $\hbar^2/2\mu\, R_0^2$.

Problem 12. A hydrogen atom is subject to a constant electric field in the z-direction (Stark effect):

1. Construct the matrix of the perturbation for the $n = 2$ state and diagonalize this matrix.
2. Do the same for the $N = 2$ states of the harmonic oscillator potential.

Problem 13. Consider N fermions interacting through $V = \frac{\zeta}{4} \sum_{i,j} (x_i - x_j)^2$:

1. Write the Hamiltonian H in second quantization form.
2. Write the Hartree Hamiltonian H_{H} and the residual interaction V'. Find the Hartree frequency ω_{H}.
3. Write the RPA Hamiltonian H_{RPA} and find the root ω_{RPA} ($N \gg 1$).
4. Which symmetry is carried by the original Hamiltonian H and is violated by H_{H} (see Chap. 10).