Chapter 7

The Linear $E \otimes e$ Jahn–Teller and Pseudo Jahn–Teller Hamiltonians

The linear $E \otimes e$ Jahn–Teller (JT) and pseudo Jahn–Teller (PJT) Hamiltonians are of topical interest in the field of quantum chemistry, and, in this chapter, we therefore discuss the relevance of these Hamiltonians in this field. We present a representation–independent operator approach to the numerical diagonalization of H_{JT} and H_{PJT} which also simplifies the analysis of the isolated exact (Juddian) solutions for these models. In particular, we give a simple closed form for the analytic ground–state wave function of the linear $E \otimes e$ resonant pseudo Jahn–Teller (RPJT) Hamiltonian. An analysis of the ground–state behaviour of the linear $E \otimes e$ JT and PJT models is also presented. Finally, we review the results of some earlier approximate

many–body analyses of these systems. The application of the CCM to the linear $E \otimes e$ JT and PJT Hamiltonians forms the subject of Chapter 8, and is therefore not discussed here.

7.1 Discussion of the Hamiltonians

The linear $E \otimes e$ PJT Hamiltonian

$$\begin{aligned} H_{\rm PJT} &= \frac{1}{2}\omega_0\,\sigma^z + \omega\,N_b + \eta\,\left(b_1^\dagger + b_1\right)\sigma^x - \eta\,\left(b_2^\dagger + b_2\right)\sigma^y \\ &= \frac{1}{2}\omega_0\,\sigma^z + \omega\,N_b + \gamma\,\left(a_1 + a_2^\dagger\right)\sigma^+ + \gamma\,\left(a_1^\dagger + a_2\right)\sigma^-, \end{aligned} \tag{7.1}$$

with $\gamma \equiv \eta/\sqrt{2}$ and the bosonic number operator N_b defined by

$$N_b \equiv b_1^\dagger b_1 + b_2^\dagger b_2 = a_1^\dagger a_1 + a_2^\dagger a_2\,, \tag{7.2}$$

was introduced in Chapter 2. The bosonic creation and annihilation operators in the first (second) line of (7.1) refer to modes of linear (circular) polarization, and the zero–point energy ω of these two modes has been neglected. The (pure) linear $E \otimes e$ JT Hamiltonian

$$\begin{aligned} H_{\rm JT} &= \omega\,N_b + \eta\,\left(b_1^\dagger + b_1\right)\sigma^x - \eta\,\left(b_2^\dagger + b_2\right)\sigma^y \\ &= \omega\,N_b + \gamma\,\left(a_1 + a_2^\dagger\right)\sigma^+ + \gamma\,\left(a_1^\dagger + a_2\right)\sigma^-, \end{aligned} \tag{7.3}$$

may formally be regarded as the special case of $H_{\rm PJT}$ where the two fermionic levels are degenerate ($\omega_0 = 0$). Both $H_{\rm JT}$ and $H_{\rm PJT}$ have the symmetries

$$\Pi_{\rm PJT} = \Pi_{\rm JT} = \exp\left\{i\pi\left[N_b + \frac{1}{2}\left(\sigma^z + 1\right)\right]\right\} \tag{7.4}$$

and

$$J = i\left(b_1^\dagger b_2 - b_1 b_2^\dagger\right) + \frac{1}{2}\sigma^z = a_1^\dagger a_1 - a_2^\dagger a_2 + \frac{1}{2}\sigma^z\,, \tag{7.5}$$

where the expression in terms of operators referring to modes of circular polarization highlights the physical meaning of the angular momentum component J in terms of helicity. It is clear that the eigenvalues of J are elements of the set $\left\{\ldots, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\right\}$.

7.1.1 Vibronic interactions and non–adiabaticity in quantum chemistry

The linear $E \otimes e$ JT and PJT Hamiltonians are clearly relevant in quantum optics, where they describe a simple extension of the Rabi Hamiltonian to the case of two degenerate perpendicularly polarized field modes. The Hamiltonians can also be used to model a two–level fermion moving in a circular ring which can undergo elliptical deformation in a plane [Lo58]. Both Hamiltonians, and H_{JT} in particular, have however been extensively studied in quantum chemistry [Bera, Berb], and we present here an introduction to non–adiabatic models in this field.

One of the most important simplifications of the Schrödinger equation for the electrons and nuclei in a molecular system is the separation of their respective motions in the adiabatic approximation [Bo27, Bor]. Based on the mass difference between an electron and a typical nucleus, it is assumed in this approximation that every instantaneous (fixed) configuration Q of the nuclei corresponds to a set of stationary electronic states. The Q–dependent (or so-called vibronic) electron–nuclear interactions which couple different electronic states are ignored, and each electronic energy eigenvalue is used

to construct a corresponding adiabatic potential (also known as a potential–energy surface [Mo87]). The adiabatic potential represents the potential energy of the nuclei in the mean field of the electrons in the corresponding electronic state, and the molecular structure for this state is determined by finding the nuclear configuration Q_0 which minimizes the adiabatic potential.

Landau argued [Berb] that, in the adiabatic approximation, a given symmetric nuclear configuration Q_s would be unstable if any of the corresponding electronic states were degenerate, and that the degeneracy would result in nuclear displacements which destroy the symmetry of Q_s. This statement is not entirely correct. For a system where n sheets of the adiabatic potential intersect (corresponding to n–fold electronic degeneracy) at a particular nuclear configuration Q^*, it is true that at least one of these sheets does not have an extremum at the point Q^* — this is the essence of the Jahn–Teller theorem [Ja37, Berb]. However, the adiabatic potential in the neighbourhood of the point of instability, Q^*, cannot be interpreted as the potential energy of the nuclei in the mean field of the electrons, and therefore cannot be used to draw conclusions about the nuclear behaviour. Rather, the correct conclusion is that the instability at Q^* implies that it is necessary to reexamine the validity of the adiabatic potential in this region.

For the nuclear motion to be localized about a given minimal configuration Q_0, the quantum ω of small nuclear vibrations about Q_0 should not allow for tunneling through the potential barrier (centered at the point Q^*) separating Q_0 from other minima. A criterion for the applicability of the

adiabatic approximation is therefore given by [Bera]

$$\omega \ll |\epsilon_n - \epsilon_k| \ , \tag{7.6}$$

where ϵ_i denotes the eigenenergy of the i–th electronic state, calculated at the point Q_0. If this condition is satisfied, the physical implication is that the adiabatic approximation is self–consistent, *i.e.* that the molecular system may be modelled as a combination of stable electronic states and localized vibrational nuclear states. If condition (7.6) is not satisfied, it is necessary to go beyond the adiabatic approximation. This requires the consideration of the vibronic electron–nuclear interactions, which couple the electronic states of the adiabatic approximation as a function of the nuclear configuration Q, and the resultant effect on the nuclear dynamics is known as the dynamical JT effect. The linear (quadratic) dynamical JT effect occurs when the vibronic interaction terms, expanded in powers of Q, are truncated at first (second) order in Q.

The linear $E \otimes e$ JT Hamiltonian $H_{\rm JT}$ represents a simple non–adiabatic molecular model of the vibronic interaction between a two–fold degenerate electronic level (E) and two degenerate nuclear vibrational modes (e). The bosonic quanta corresponding to the vibrational modes are thus phonons. In the case of electronic near–degeneracy, non–adiabatic (pseudo Jahn–Teller) effects also occur if the electronic level splitting ω_0 is comparable to the nuclear vibrational excitation energy ω. We therefore also consider the linear $E \otimes e$ PJT Hamiltonian $H_{\rm PJT}$, which generalizes the (pure) JT model to the case of nondegenerate electronic levels. In both cases it is assumed that the two levels under consideration are well separated from other electronic levels.

7.1.2 Analytic solutions in the limit of zero coupling

In the analysis of a Hamiltonian describing an interacting many–body system, the eigenbasis of the noninteracting Hamiltonian is often useful both for TIPT and the CI (diagonalization) method. The linear $E \otimes e$ JT and PJT Hamiltonians are analytic in the limit of zero coupling γ. Consider the noninteracting JT Hamiltonian $H_{\rm JT}^{\gamma=0} \equiv \omega N_b$. The exact ground states of $H_{\rm JT}^{\gamma=0}$ are the states $|0\rangle|0\rangle|\downarrow\rangle$ and $|0\rangle|0\rangle|\uparrow\rangle$, where in each case the first (second) ket refers to the bosonic occupation number vacuum for the first (second) bosonic mode, and the third ket denotes the lower ($|\downarrow\rangle$) or upper ($|\uparrow\rangle$) level of the fermionic mode. For $\gamma = 0$ these states are degenerate with ground–state energy $E_{\rm JT}^{\gamma=0} = 0$. The state $|0\rangle|0\rangle|\downarrow\rangle$ ($|0\rangle|0\rangle|\uparrow\rangle$) is of positive (negative) $\Pi_{\rm PJT}$ parity and corresponds to angular momentum component $j = -1/2$ ($j = 1/2$). The complete spectrum of $H_{\rm JT}^{\gamma=0}$ is simply determined; the n–th excited level has energy $E_n = n\omega$ and is $2\,(n+1)$–fold degenerate. The factor 2 arises from the electronic degeneracy, and there are $(n+1)$ ways to distribute the n bosonic quanta over the two modes.

In the limit of zero coupling the noninteracting PJT Hamiltonian

$$H_{\rm PJT}^{\gamma=0} \;=\; \frac{1}{2}\omega_0\,\sigma^z \;+\; \omega N_b \;, \qquad (\omega_0 > 0) \tag{7.7}$$

has the exact ground state $|0\rangle|0\rangle|\downarrow\rangle$, which uniquely corresponds to the ground–state energy $E_{\rm PJT}^{\gamma=0} = -\omega_0/2$. Here the ground state is thus of positive $\Pi_{\rm PJT}$ parity, and has angular momentum component $j = -1/2$. The determination of the complete spectrum of $H_{\rm PJT}^{\gamma=0}$, which is dependent on the relative magnitudes of ω and ω_0, is straightforward.

7.1.3 Numerical diagonalization of the JT and PJT models

Although there is strong numerical support for the conjecture of Reik *et.al.* [Re87], and although the linear $E \otimes e$ JT and PJT Hamiltonians have furthermore been written in canonical form [Sz97], the integrability of these models for arbitrary coupling γ and fermionic level splitting ω_0 has not been explicitly demonstrated. We therefore turn to the CI method, which involves the numerical diagonalization of the Hamiltonian in a finite subspace of the full Hilbert space.

For $\gamma > 0$, the Hamiltonian H_{PJT} (for arbitrary ω_0 and thus including the JT case $\omega_0 = 0$) does not commute with the bosonic number operator N_b, and the noninteracting eigenbasis is no longer the most appropriate basis for the diagonalization of the Hamiltonian. Rather, since the operators H_{PJT}, J and Π_{PJT} form a mutually commuting set, the matrix representation of H_{PJT} in a simultaneous eigenbasis of J and Π_{PJT} blocks into sectors corresponding to fixed eigenvalue j of the operator J and either positive or negative Π_{PJT}–parity. This not only results in a considerable reduction in the numerical effort involved in the diagonalization of the Hamiltonian, but also, as we will show, yields an explanation of the two–fold degeneracy of all energy levels in the spectrum of the linear $E \otimes e$ JT Hamiltonian.

We present here an operator–based approach to the construction of an appropriate simultaneous eigenbasis of the operators J and Π_{PJT}. We introduce the operator $c^\dagger$ and its Hermitian conjugate c via

$$c^\dagger \equiv \frac{1}{\sqrt{2}}\left(b_1^\dagger\sigma^x - b_2^\dagger\sigma^y\right) = \frac{1}{2}\left(a_2^\dagger\sigma^+ + a_1^\dagger\sigma^-\right)$$
$$c = \frac{1}{\sqrt{2}}\left(b_1\sigma^x - b_2\sigma^y\right) = \frac{1}{2}\left(a_2\sigma^- + a_1\sigma^+\right) . \quad (7.8)$$

It is easily shown that

$$[c, J] = \left[c^\dagger, J\right] = 0$$
$$[c, \Pi_{\rm PJT}] = \left[c^\dagger, \Pi_{\rm PJT}\right] = 0 , \quad (7.9)$$

and also that

$$\left(c^\dagger\right)^2 = \frac{1}{2}\left[\left(b_1^\dagger\right)^2 + \left(b_2^\dagger\right)^2\right] = a_1^\dagger a_2^\dagger . \quad (7.10)$$

The Hamiltonian $H_{\rm PJT}$ may, for arbitrary ω_0, be rewritten as

$$H_{\rm PJT} = \frac{1}{2}\omega_0\,\sigma^z + \omega\, N_b + 2\gamma\, c^\dagger + 2\gamma\, c , \quad (7.11)$$

where the bosonic number operator N_b assumes the form

$$N_b = 2\, c^\dagger c + J\sigma^z - \frac{1}{2} . \quad (7.12)$$

Here $J\sigma^z = cc^\dagger - c^\dagger c - \frac{1}{2}$, and the parity operator $\Pi_{\rm PJT}$ retains the form (7.4). The operators c, $c^\dagger$ and σ^z obey the relations [1]

$$\left[c, \left(c^\dagger\right)^{2n}\right] = n\left(c^\dagger\right)^{2n-1} , \qquad \left[c, \left(c^\dagger\right)^{2n+1}\right] = \left(c^\dagger\right)^{2n}\left(J\sigma^z + n + \frac{1}{2}\right)$$
$$\left[\sigma^z, c^{2n}\right] = \left[\sigma^z, \left(c^\dagger\right)^{2n}\right] = \left[\sigma^z, c^{2n+1}\right]_+ = \left[\sigma^z, \left(c^\dagger\right)^{2n+1}\right]_+ = 0 \quad (7.13)$$

for $n = 0, 1, 2, \ldots$. It then follows that

$$\left[N_b, \left(c^\dagger\right)^n\right] = n\left(c^\dagger\right)^n , \qquad [c, N_b] = c \quad (7.14)$$

[1] The subscript + denotes an anticommutator.

and, as expected,

$$[J, \sigma^z] = [J, N_b] = 0 \, . \tag{7.15}$$

Consider an arbitrary j–sector, which is an infinite–dimensional subspace of the full Hilbert space. We postulate that the requirement

$$c|\Psi\rangle_j^{\text{ref}} = 0 \tag{7.16}$$

uniquely determines the state $|\Psi\rangle_j^{\text{ref}}$, which is a reference state of angular momentum component j that will be used as a starting vector for the construction of a suitable basis for this sector. Using (7.13), one obtains

$$c\left\{\sigma^z|\Psi\rangle_j^{\text{ref}}\right\} = -\sigma^z c|\Psi\rangle_j^{\text{ref}} = 0 \, , \tag{7.17}$$

and from (7.15) it follows that the state $\left\{\sigma^z|\Psi\rangle_j^{\text{ref}}\right\}$ is also an eigenstate of J with eigenvalue j. The assumed uniqueness of $|\Psi\rangle_j^{\text{ref}}$ implies that the reference state must therefore be an eigenstate $|\Psi\rangle_{j,s}^{\text{ref}}$ of σ^z with eigenvalue $s \in \{-1, 1\}$. It follows from a similar argument using (7.14) and (7.15) that the reference state must also be an eigenstate of the bosonic number operator N_b with eigenvalue $n_b \in \{0, 1, 2, \ldots\}$. Using the form (7.12) and the requirement (7.16), it is clear that

$$n_b \; = \; j\, s \; - \; \frac{1}{2} \geq 0 \, , \tag{7.18}$$

and also that

$$\Pi_{\text{PJT}} \, |\Psi\rangle_{j,s}^{\text{ref}} \; = \; \exp\left[i\pi \left(j + \frac{1}{2}\right) s\right] \, |\Psi\rangle_{j,s}^{\text{ref}} \, . \tag{7.19}$$

There are now two possibilities:

1. The eigenvalue j is positive, so that $j = p + 1/2$ with $p \in \{0, 1, 2, \ldots\}$. In this case, condition (7.18) implies that $s = 1$ and $n_b = p$, and

we deduce from (7.19) that the reference state $|\Psi\rangle^{\rm ref}_{j=p+1/2,s=1}$ for this positive–j sector is of even (odd) $\Pi_{\rm PJT}$–parity for p odd (even).

2. The eigenvalue j is negative, so that $j = -p - 1/2$ with $p \in \{0, 1, 2, \ldots\}$. In this case, condition (7.18) implies that $s = -1$ and $n_b = p$, and we deduce from (7.19) that the reference state $|\Psi\rangle^{\rm ref}_{j=-p-1/2,s=-1}$ for this negative–j sector is of even (odd) $\Pi_{\rm PJT}$–parity for p even (odd).

Clearly $js = p + 1/2$ in both cases. Given the eigenvalue $j = \pm(p + 1/2)$, the condition (7.16) therefore fully determines the reference state $|\Psi\rangle^{\rm ref}_{j,s}$. For example, in the occupation number representation of modes of circular polarization, the reference state for the $j = p + 1/2$–sector is $|p\rangle|0\rangle|\uparrow\rangle$, and that for the $j = -p - 1/2$–sector is $|0\rangle|p\rangle|\downarrow\rangle$. These examples clearly illustrate the role of the reference state as the "simplest" state in the given sector.

The operator approach now allows for the construction of a suitable basis for this j–sector, without the need to specify the explicit form of the basis states in terms of *e.g.* linearly of circularly polarized bosonic modes. For an arbitrary j–sector eigenstate $|\Psi\rangle_j$ of $H_{\rm RPJT}$, we construct the power series expansion

$$|\Psi\rangle_j \;=\; \sum_{n=0}^{\infty} X_n \left(c^\dagger\right)^n |\Psi\rangle^{\rm ref}_{j,s} \,. \tag{7.20}$$

Since $c^\dagger$ commutes with both J and $\Pi_{\rm PJT}$, it is clear that the state $|\Psi\rangle_j$ has the same J and $\Pi_{\rm PJT}$ quantum numbers as the reference state $|\Psi\rangle^{\rm ref}_{j,s}$. Substituting the expansion (7.20) into the Schrödinger equation

$$H_{\rm PJT}|\Psi\rangle_j = E|\Psi\rangle_j \,, \tag{7.21}$$

and using the relations (7.13), (7.14) and the condition (7.16), one obtains

for the coefficients $\{X_i\}$ the recurrence relations

$$\begin{aligned} 0 &= 2\gamma X_{2n-1} + \left[(p+2n)\omega + s\frac{1}{2}\omega_0 - E\right] X_{2n} + 2\gamma(p+n+1)X_{2n+1} \\ 0 &= 2\gamma X_{2n} + \left[(p+2n+1)\omega - s\frac{1}{2}\omega_0 - E\right] X_{2n+1} + 2\gamma(n+1)X_{2n+2} \end{aligned} \quad (7.22)$$

where $s = 1$ for $j = p + 1/2$ and $s = -1$ for $j = -p - 1/2$. These equations constitute a simple reformulation of the Longuet–Higgins recurrence relations [Lo58, Ju79, Re81a], generalized to incorporate the case $\omega_0 > 0$. The solution of these recurrence relations is equivalent to the diagonalization of the tri–diagonal matrix representation of H_{PJT} in the j–sector,

$$\begin{bmatrix} p\,\omega + \frac{s}{2}\omega_0 & 2\gamma\sqrt{p+1} & 0 & 0 & 0 & \dots \\ 2\gamma\sqrt{p+1} & (p+1)\,\omega - \frac{s}{2}\omega_0 & 2\gamma\sqrt{1} & 0 & 0 & \dots \\ 0 & 2\gamma\sqrt{1} & (p+2)\,\omega + \frac{s}{2}\omega_0 & 2\gamma\sqrt{p+2} & 0 & \dots \\ 0 & 0 & 2\gamma\sqrt{p+2} & (p+3)\,\omega - \frac{s}{2}\omega_0 & 2\gamma\sqrt{2} & \dots \\ 0 & 0 & 0 & 2\gamma\sqrt{2} & (p+4)\,\omega + \frac{s}{2}\omega_0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (7.23)$$

In general (*i.e.* $\omega_0 > 0$ arbitrary), the eigenvalues of the matrix (7.23) will be different for the cases $s = \pm 1$, and the eigenstates of H_{PJT} are thus singlet states of definite parity and angular momentum component j. In particular, the ground state of H_{PJT} is a unique positive–parity state, corresponding to $j = -1/2$, for all values of the coupling γ. Since the Longuet–Higgins relations (7.22) are invariant under the simultaneous replacements $\{\omega_0 \to -\omega_0, j \to -j, s \to -s\}$, it is clear that the first excited state of H_{PJT}, which is a unique negative–parity state corresponding to $j = 1/2$ and $s = 1$, may be obtained by replacing ω_0 by $-\omega_0$.

The matrix representation of the linear $E \otimes e$ JT Hamiltonian H_{JT} in the j–sector is obtained by setting $\omega_0 = 0$ in (7.23). The representations

of H_{JT} in the $j = p + 1/2$ and $j = -p - 1/2$–sectors (which are of opposite parity) are therefore identical, which explains the two–fold degeneracy of all energy levels in the spectrum of the linear $E \otimes e$ JT Hamiltonian. In particular, the diagonalization of (7.23) for $\{\omega_0 = 0; p = 0, j = -1/2\}$ and $\{\omega_0 = 0; p = 0, j = 1/2\}$ yields the energy of the positive– and negative–parity ground states of H_{JT}, which are degenerate for all couplings. Thus the inclusion of the (vibronic) interaction terms transforms the electronic degeneracy of the noninteracting ground state of H_{JT} into a parity degeneracy (also referred to as a vibronic degeneracy [Berb]) at finite coupling. In the H_{PJT} model, the finite fermionic level splitting ω_0 lifts the parity degeneracy of the ground state for all values of the coupling, and the Hamiltonian H_{PJT} is in this sense analogous to the Rabi Hamiltonian.

For the Hamiltonian H_{JT}, *i.e.* for $\omega_0 = 0$, the numerical diagonalization of (7.23) was first performed by Longuet–Higgins *et.al.* [Lo58]). Besides the energy spectrum of the linear $E \otimes e$ JT model, the eigenvalues of the matrix (7.23) with $\omega_0 = 0$ also yield the energies of the linear $\Gamma_8 \otimes \tau_2$ JT model. However, for this model, which describes the vibronic interactions between a fourfold–degenerate electronic state and a triply–degenerate nuclear vibrational mode, the quantum number p is replaced by the quantity m, which assumes half–integer rather than integer values. Numerical results for the energy levels of the linear $\Gamma_8 \otimes \tau_2$ JT Hamiltonian were presented by Thorson and Moffit [Th68].

7.1.4 Juddian solutions for the JT and PJT models

As is the case for the Rabi Hamiltonian, analytic solutions for some of the energy eigenvalues of the Hamiltonians $H_{\rm JT}$ and $H_{\rm PJT}$ occur at isolated values of the coupling γ. Using algebraic methods, Judd [Ju79, Ju77] showed that, for both the linear $\Gamma_8 \otimes \tau_2$ and linear $E \otimes e$ JT models, rational eigenvalues occur at isolated values of γ where the Longuet–Higgins recurrence relations can be solved in closed form. Reik *et.al.* [Re81a, Re81b, Re81c, Re82] simplified the analysis of these Juddian solutions by reformulating the eigenvalue problem for both models in Bargmann's space of analytical functions, and extended the search for Juddian solutions to the Rabi and linear $E \otimes e$ PJT Hamiltonians [Re82]. The important contribution of Reik *et.al.* is the observation that, at the Juddian points, a Neumann expansion of the wave function in modified Bessel functions terminates after a finite number of terms. This allows for the systematic and (at least in principle) straightforward determination, in closed form, of the values of the coupling γ and energy E at the Juddian points.

Here we rederive the results of Reik *et.al.* using the operator approach introduced in the previous section. Our motivation is threefold: the equations which determine the Juddian values of the coupling and energy are more simply derived in this approach; the operator $c^\dagger$, which obeys the relation (7.10), plays the role of the the Bargmann number $\sqrt{z}$ in [Re82], and therefore allows for the construction of explicit expressions for the Juddian wave functions in the Dirac rather than the Bargmann representation; finally, the operator approach yields results which are independent of the explicit realization of

the bosonic modes. By analogy with the approach in [Re82], we therefore construct the following (unnormalized) Neumann expansion for $|\Psi\rangle_j$:

$$\begin{aligned} |\Psi\rangle_j &= \sum_{n=0}^{\infty} \frac{x_n}{\kappa^{4n} n!} \left(\kappa c^\dagger\right)^{n-p} I_{n+p}\left(2\kappa c^\dagger\right) |\Psi\rangle_{j,s}^{\text{ref}} \\ &\quad + \sum_{n=0}^{\infty} \frac{y_n}{\kappa^{4n} n!} \left(\kappa c^\dagger\right)^{n-p} I_{n+p+1}\left(2\kappa c^\dagger\right) |\Psi\rangle_{j,s}^{\text{ref}}, \end{aligned} \tag{7.24}$$

where $\kappa \equiv \gamma/\omega$, I_n is a modified Bessel function of the first kind of order n (see *e.g.* [Abr]), and as before $s = 1$ ($s = -1$) for $j = p + 1/2$ ($j = -p - 1/2$). Then

$$\begin{aligned} |\Psi\rangle_j &= \sum_{n=0}^{\infty} \frac{x_n}{\kappa^{4n} n!} \sum_{k=0}^{\infty} \frac{\left(\kappa c^\dagger\right)^{2n+2k}}{k!(p+n+k)!} |\Psi\rangle_{j,s}^{\text{ref}} \\ &\quad + \sum_{n=0}^{\infty} \frac{y_n}{\kappa^{4n} n!} \sum_{k=0}^{\infty} \frac{\left(\kappa c^\dagger\right)^{2n+2k+1}}{k!(p+n+k+1)!} |\Psi\rangle_{j,s}^{\text{ref}}. \end{aligned} \tag{7.25}$$

Substituting (7.25) into the Schrödinger equation (7.21) we obtain for $n = 0, 1, 2, \ldots$,

$$\begin{aligned} 0 &= \left\{\frac{p}{2} + n + s\frac{\omega_0}{4\omega} - \frac{E}{2\omega}\right\} x_n + \kappa^2 y_n + n\kappa^4 \left(x_{n-1} + y_{n-1}\right) \\ 0 &= \frac{1}{\kappa^2} x_{n+1} + \left\{\frac{p}{2} + n + \frac{1}{2} - s\frac{\omega_0}{4\omega} - \frac{E}{2\omega}\right\} y_n \\ &\quad + \left\{p + n + 1 + \kappa^2\right\} x_n + n\kappa^4 \left(x_{n-1} + y_{n-1}\right) , \end{aligned} \tag{7.26}$$

where by definition $x_{-1} = y_{-1} = 0$. Elimating $x_{n-1} + y_{n-1}$ from the recurrence relations (7.26), and introducing the parameters δ and v via

$$\begin{aligned} \delta &\equiv \frac{\omega_0 - \omega}{4\omega} \\ E &\equiv \left(v - \frac{1}{2} - 2\kappa^2\right)\omega , \end{aligned} \tag{7.27}$$

one obtains, for the case $j = -p - 1/2$ where $s = -1$,

$$\begin{bmatrix} x_{n+1} \\ y_{n+1} \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} x_n \\ y_n \end{bmatrix} \quad n = 0, 1, 2, \ldots,$$

$$
\begin{aligned}
M_{11} &= -\kappa^2\left(\frac{p}{2}+1+\delta+\frac{v}{2}\right) \\
M_{12} &= -\kappa^2\left(\frac{p}{2}+1+\delta+n-\frac{v}{2}\right) \\
M_{21} &= \left(\kappa^2+\frac{p}{2}+1-\delta+n-\frac{v}{2}\right)\left(\frac{p}{2}+1+\delta+\frac{v}{2}\right)-\kappa^2\,(n+1) \\
M_{22} &= \left(\kappa^2+\frac{p}{2}+1-\delta+n-\frac{v}{2}\right)\left(\frac{p}{2}+1+\delta+n-\frac{v}{2}\right)-\kappa^2\,(n+1), \qquad (7.28)
\end{aligned}
$$

with the initial condition

$$
\kappa^2 y_0 = -\left(\kappa^2+\frac{p}{2}-\delta-\frac{v}{2}\right)x_0\,. \qquad (7.29)
$$

The parameter x_0 simply fixes the norm of $|\Psi\rangle_{-p-1/2}$. For an eigenstate of H_{PJT} corresponding to the positive J eigenvalue $j = p + 1/2$, a similar analysis with $s = 1$ yields equations identical in form to (7.28), but with δ replaced by $-\delta - 1/2$, or equivalently with ω_0 replaced by $-\omega_0$. Taking $x_0 = \kappa^2$ and $s = 1$, Equations (7.28) and (7.29) become identical to Equations (3.4–3.8) and (3.11), respectively, of [Re82], so that the correspondence between (7.24) and the Bargmann analysis of [Re82] is complete.

The derivation of (7.28) is valid for arbitrary ω_0, including the JT case $\omega_0 = 0$. Furthermore, it can be shown [Re82] that, in the case $p = -1/2$, the solution of (7.28) yields the energy eigenvalues $E = (v - 2\kappa^2)\,\omega$ of the Rabi Hamiltonian. Thus the set of equations (7.28) are to be solved for both δ and $\delta \to -\delta - 1/2$, and in each case for arbitrary nonnegative integers p as well as for $p = -1/2$.

Juddian solutions for H_{JT}, H_{PJT} and H_{Rabi} occur whenever the Neumann series (7.24) terminates at finite order; such a termination occurs at the N-th term if and only if both the conditions $v = N$ and $\Sigma_N \equiv x_N + y_N = 0$

are met [Re82]. By (7.27), the condition $v = N$ ensures that the energy corresponding to these solutions lies on the Nth baseline, defined for the JT and PJT systems by

$$E_N^{\text{Baseline}} = \left(N - \frac{1}{2} - 2\kappa^2\right)\omega = \left(N - \frac{1}{2}\right)\omega - \frac{2\gamma^2}{\omega} \,. \tag{7.30}$$

The quantity Σ_N is a polynomial of degree N in κ^2. For given values of the parameters p and δ, the conditions $v = N, \Sigma_N = 0$ therefore algebraically determine the values of the coupling for which Juddian solutions on the N-th baseline exist.

For $v = N = 0$, the condition $\Sigma_0 = x_0 + y_0 = 0$ reduces to

$$p^* - 2\delta^* = 0 \,, \tag{7.31}$$

which is independent of the coupling κ, and thus yields an analytic solution, valid for all coupling, for $p = p^*, \delta = \delta^*$. The case $p^* = -1/2, \delta^* = -1/4$, which refers to the Rabi Hamiltonian with degenerate atomic levels, was discussed in Chapter 4. Here we consider also the case of the linear $E \otimes e$ resonant ($\omega_0 = \omega$) pseudo Jahn–Teller Hamiltonian H_{RPJT}, for which $\delta = 0$. For H_{RPJT}, the condition (7.31) is therefore satisfied for $p^* = 0$, which corresponds to the negative J eigenvalue $j^* = -p^* - 1/2 = -1/2$ and $s = -1$. In this case the reference state $|\Psi\rangle_{j,s}^{\text{ref}}$ has the form $|0\rangle|0\rangle|\downarrow\rangle$, where $|0\rangle|0\rangle$ is the bosonic vacuum for any particular realization of the bosonic modes. Thus we find that the ground ($j = -1/2$) state $|\Psi_0^{\text{RPJT}}\rangle$ of the RPJT Hamiltonian

$$\begin{aligned} H_{\text{RPJT}} \;=\; & \frac{1}{2}\omega\,\sigma^z \;+\; \omega\, a_1^\dagger a_1 \;+\; \omega\, a_2^\dagger a_2 \\ & + \gamma\,\left(a_1 + a_2^\dagger\right)\sigma^+ \;+\; \gamma\,\left(a_1^\dagger + a_2\right)\sigma^- \end{aligned} \tag{7.32}$$

assumes the closed form

$$|\Psi_0^{\mathrm{RPJT}}\rangle = A_{\mathrm{RPJT}} \left\{ I_0\left(2\kappa c^\dagger\right) - I_1\left(2\kappa c^\dagger\right) \right\} |0\rangle|0\rangle|\downarrow\rangle \,, \tag{7.33}$$

where A_{RPJT} is a normalization constant, and the corresponding ground–state energy is

$$E_0^{\mathrm{RPJT}} = E_0^{\mathrm{Baseline}} = -\frac{1}{2}\omega - \frac{2\gamma^2}{\omega} \,. \tag{7.34}$$

This solution, which is analytic for all coupling γ, clearly highlights the advantages of the operator approach. Expressed in terms of bosonic modes of circular polarization, $|\Psi_0^{\mathrm{RPJT}}\rangle$ assumes the explicit form

$$|\Psi_0^{\mathrm{RPJT}}\rangle = A_{\mathrm{RPJT}} \sum_{k=0}^{\infty} \left\{ \frac{\kappa^{2k}}{\sqrt{k!k!}} |k\rangle|k\rangle|\downarrow\rangle - \frac{\kappa^{2k+1}}{\sqrt{k!(k+1)!}} |k\rangle|k+1\rangle|\uparrow\rangle \right\} , \tag{7.35}$$

which allows for the determination of A_{RPJT} via

$$\begin{aligned} A_{\mathrm{RPJT}} &= \left\{ \sum_{k=0}^{\infty} \left(\frac{\kappa^{4k}}{k!k!} + \frac{\kappa^{4k+2}}{k!(k+1)!} \right) \right\}^{-1/2} \\ &= \left\{ I_0\left(2\kappa^2\right) + I_1\left(2\kappa^2\right) \right\}^{-1/2} \,. \end{aligned} \tag{7.36}$$

For $v = N > 0$, the conditions $\Sigma_N = x_N + y_N = 0$ may be used to find other Juddian solutions for H_{Rabi}, H_{JT}, and H_{PJT}. It has been conjectured [Re87] that an expansion of the wave function in generalized spheroidal functions terminates at all values of the coupling, rather than only at the Juddian points. Despite very strong numerical evidence, this conjecture has not been proved. However, the Juddian solutions may be still used to gauge the accuracy of approximate many–body techniques, even if only at isolated values of the coupling. In particular, the converged CI (diagonalization) results for the spectra of H_{JT} and H_{PJT} can be shown to be exact for all practical

purposes. Also, it can be shown [Re81a] that, for large coupling γ, all eigenvalues of $H_{\rm JT}$ and $H_{\rm PJT}$ approach the baselines (7.30). In particular, both the ground and first excited state energies of these Hamiltonians approach the value $E_0^{\rm Baseline} = E_0^{\rm RPJT} = -\omega/2 - 2\gamma^2/\omega$ in the limit $\gamma \to \infty$.

7.2 Physical characteristics of the JT and PJT ground states

The ground–state behaviour of the linear $E \otimes e$ JT and PJT Hamiltonians is analogous to that of the Rabi ground state, in that a marked change in character occurs in the ground state in the intermediate coupling regime. Again, this character change manifests itself in the ground–state expectation value of the operator σ^z, which is readily evaluated using the CI method. In the ground state of H_{PJT} with $\omega_0 > 0$, the fermion is more likely to be found in the lower state for small coupling, and (almost) equally likely to be found in either the upper or lower state at large coupling. The crossover between these two regimes, though not discontinuous, takes place in a fairly well–defined region of coupling, which is dependent on the the fermionic level splitting ω_0. For H_{JT}, the same behaviour is observed, provided that the ground state is restricted to, say, even $\Pi_{\rm PJT}$ parity (or equivalently to the negative J eigenvalue $j = -1/2$). Thus, as before, one may use the expectation value $\langle\sigma^z\rangle$ or, more effectively, the fluctuation $\Delta\sigma^z$, to identify the transitional coupling region.

The physical nature of the crossover observed here may be seen by examining the behaviour of the ground state of the (part of a) molecular system described by either the JT or PJT Hamiltonian, for large values of the scaled coupling κ. Consider first the simpler Hamiltonian H_{JT}. Denoting the energy gap between the two sheets of the adiabatic potential corresponding to the ground state by $\Delta(Q)$, it is readily shown that $\Delta_0 \equiv \Delta(Q_0) \approx 8\omega\kappa^2$, where Q_0 represents the minimum–energy nuclear configuration [Berb]. For large κ, it is evident that Δ_0 is much larger than the nuclear vibrational quantum ω. Thus the criterion (7.6) is satisfied, and the lower sheet of the adiabatic potential may be interpreted as the ground–state potential energy of the nuclei in the average field of the electrons. Quantizing the motion of the nuclei in this potential, one obtains the observed form (7.34) of the ground–state energy for large coupling [Berb]. The criterion $\Delta_0 \sim \omega$ provides a simple measure of the onset of this type of ground–state behaviour, so that we expect a change in character of the ground state of H_{JT} at

$$\kappa^{\mathrm{trans}} \sim \frac{1}{\sqrt{8}} . \tag{7.37}$$

This is in good agreement with the transitional coupling region for H_{JT} identified by considering the behaviour of $\Delta\sigma^z$. Although the finite fermionic level splitting ω_0 in the linear $E \otimes e$ PJT model affects the shape of the adiabatic potentials, the ground–state behaviour for large coupling is similar to that described above for H_{JT} [Berb], and a similar transitional region is observed.

7.3 Approximate many–body approaches to the JT and PJT models

The approach outlined in Section 7.2 above may be used [Berb] to obtain quantitatively accurate results for the spectrum of both H_{JT} and H_{PJT} in the limit of large coupling γ. Accurate results for these models can also be obtained in the opposite limit of small γ, using an operator version of time–independent perturbation theory (see [Bera, Berb] and references therein). For both H_{JT} and H_{PJT}, however, physically realistic values of the vibronic interaction constant mostly correspond to the region of intermediate coupling [Berb], where quasi–analytic results cannot be obtained.

In the intermediate coupling regime, accurate results for the spectra of the Hamiltonians H_{JT} and H_{PJT} can be found using quasi–exact numerical methods such as the CI (diagonalization) approach. Generally, however, these methods do not provide much physical insight into the nature of the solution, and a variety of other many–body techniques have therefore been applied to the linear $E \otimes e$ JT and PJT models, with the bulk of the work being done on the former. Most of these calculations have involved either variational techniques (see [Berb, Lo91] and references therein), or some form of unitary transformation (see *e.g.* [Fu61]). In many cases, these methods are used in combination; recent examples include a variational calculation based on a correlated squeezed state [Lo91] for H_{JT}, and a similar calculation for H_{PJT} [Hu98]. None of these calculations, however, yield quantitatively accurate results in the physically interesting region of intermediate coupling. As

is always the case, the failure of the variational method can be attributed to a shortcoming in the variational ansatz for the wave function. As for the method of unitary transformations (which is often just a variational shift of the Hamiltonian rather than the wave function), the transformations employed often destroy either or both of the symmetries J and Π_{PJT}. This eliminates the use of these symmetries as an aid in simplifying the solution of the H_{JT} and H_{PJT} eigenvalue problems.

Given the excellent variational results [Bi99a] obtained for the Rabi Hamiltonian via a trial state of the coherent superposition form (4.38), we have attempted to perform a variational calculation for both H_{JT} and H_{PJT} based on an analogous ansatz for the case of two bosonic modes. The resulting ansatz is not, however, a state of good j quantum number, and this calculation therefore fails at intermediate and large coupling.