Theor Chim Acta (1994) 89: 123–136

Theoretica Chimica Acta

Model calculations testing the adiabatic Born–Oppenheimer approximation and its non-adiabatic corrections

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Received October 5, 1993/Accepted April 20, 1994

Summary. Tests of the accuracy of the Born–Oppenheimer approximation, with and without non-adiabatic corrections are made on a model system of two coupled harmonic oscillators representing electronic and nuclear motion. Two couplings are considered: bilinear and biquadratic in the displacements. For the energies of sublevels of the ground state, the transition dipole moments of the lowest vibrational transition, and the transition moment in a vibrationally perturbed forbidden electronic transition, the Born–Oppenheimer result including non-adiabatic corrections agrees with the exact result up to terms quadratic in the coupling constant. In a model of near-resonance of the coupled systems, "level crossing", the adiabatic approximation fails, as is well-known. Even with inclusion of the non-adiabatic corrections the result does not agree to quadratic terms. However near resonance, with physically reasonable values, the methods give results that are very close. In all cases inclusion of the non-adiabatic terms is essential.

Key words: Born–Oppenheimer approximation – Non-adiabatic corrections

1 Introduction

Calculations of the properties of molecules are generally built upon the Born–Oppenheimer principle of the separation of the motion of light and heavy particles [1]. This is commonly done in the adiabatic approximation, with electronic wave functions found for a range of fixed nuclear configurations. The nuclear position-dependence of the electronic wave functions provides the potential function for nuclear motion.

In the outcome the system wave function is expressed as a product

$$\Psi(q, Q) = \phi(q, Q)\chi(Q), \tag{1.1}$$

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$\phi(q, Q)$, the electronic wave function, is a function of the electron coordinates q for fixed values of the nuclear coordinates Q. $\chi(Q)$ is the nuclear wave function.

In cases where it is necessary to go beyond the product (1.1) the expansion (1.2) is adopted [2, 3], giving non-adiabatic state functions,

$$\Psi(q, Q) = \sum_{n,m} c_{nm} \phi^n(q, Q) \chi_{nm}(Q), \tag{1.2}$$

where n is an electronic index, and $\chi_{nm}(Q)$ is the mth vibrational level for electronic state n.

We are concerned with the so far unresolved questions, first of the convergence of the expansion (1.2), and second whether the convergence limit is an exact solution of the complete Hamiltonian. In an approach to these problems we show that for two model Hamiltonians in a range of calculations for off-resonance problems the non-adiabatic wave function (1.2) and the "exact" solutions give results equal up to terms quadratic in the coupling constant for nuclear–electron interaction. The extent to which the adiabatic approximation (1.1) requires non-adiabatic corrections depends strongly on the physical property, and is not simply related to the relative nuclear masses and frequencies. In the limit of near-resonance of potential curves a more complex situation will be described.

The Hamiltonian for a molecule can be expressed in Eq. (1.3):

$$H = T_N + T_e + U(q, Q), \tag{1.3}$$

where T_N and T_e are the nuclear and electronic kinetic energies and $U(q, Q)$ the potential energy in terms of mass-reduced electronic and mass-weighted nuclear coordinates, respectively.

To find approximate solutions to the full Schrödinger equation

$$H\Psi(q, Q) = E\Psi(q, Q), \tag{1.4}$$

the Born–Oppenheimer principle may be applied at several levels [4, 5]. Here we take the adiabatic approximation in which we solve first an electronic equation

$$H_e \phi^{(n)}(q, Q) = E_n(Q) \phi^{(n)}(q, Q), \tag{1.5}$$

in which the electronic Hamiltonian H_e,

$$H_e = T_e + U(q, Q), \tag{1.6}$$

is given for a set, or sets, of fixed values of the nuclear coordinates Q, each specifying a molecular configuration. The solutions $\phi^n(q, Q)$ are functions of electronic coordinates for the fixed Q values, which are treated as parameters. For nuclear masses very large compared with the electron mass this is a physically realistic approximation.

For an electronic state n the wave functions for the nuclear motion are found by solving

$$(T_N + U_n(Q)) \chi_{nm}(Q) = E_{nm} \chi_{nm}(Q), \tag{1.7}$$

where

$$U_n(Q) \doteq E_n(Q) - \frac{\hbar^2}{2} \int \phi^{(n)}(q, Q) \frac{\partial^2}{\partial Q^2} \phi^{(n)}(q, Q) \, \mathrm{d}q. \tag{1.8}$$

It is generally accepted that the adiabatic approximation, where the approximation to the solutions $\Psi(q, Q)$ of the full Schrödinger equation in Eq. (1.4) is the single product given in expression (1.1), is satisfactory in the calculation of energies. For other properties, such as transition moments, circular dichroism, and vibrationally induced intensity the performance of the adiabatic approximation and its non-adiabatic corrections is not well established, though not infrequently used. Some authors employ the so-called crude adiabatic approximation [4].

It is rather striking that the closeness of the BO approximation has not been established in a general way, only by reference to particular special cases [4]. This is not surprising, given that exact solutions are not known except in the very simplest systems. In others there is nothing against which the approximate solution can be matched. It becomes attractive to seek types of coupled dynamical systems admitting exact solutions. These can be compared with solutions found in BO approximation. If there is agreement, confidence in the approximation is increased. If differences are found, their significance will need to be taken into account in dealing with molecular calculations.

The approach in this paper is to examine a model system in which both the electronic and nuclear motions are harmonic oscillators. Where these motions are uncoupled the model Hamiltonian is, now expressed in displacements x and y,

$$H_0 = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 + \frac{p_y^2}{2M} + \frac{1}{2}M\Omega^2 y^2. \tag{1.9}$$

A single electron of mass m oscillates at frequency ω and a nucleus of mass M at frequency Ω. We now introduce a coupling, so that the electron potential energy depends on the nuclear position y. This coupling is not necessarily related physically to the electrostatic force. The Hamiltonian (1.10) includes a bilinear coupling, and Eq. (1.11) a quadratic.

$$H_l = H_0 + cxy, \tag{1.10}$$

$$H_q = H_0 + \tfrac{1}{2}cm\omega^2 x^2 y^2. \tag{1.11}$$

The present work has the purpose of comparing the energy eigenvalues with and without making the Born–Oppenheimer approximation.

2 Energies of bilinearly coupled non-identical oscillators

Ground state energy in second order perturbation theory

The discussion of this case, with Hamiltonian (1.10), is a development of our earlier result [6] for coupled harmonic motions for particles of equal masses and frequencies.

The Hamiltonian (2.1),

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2M} + \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}M\Omega^2 y^2 + cxy, \tag{2.1}$$

describes harmonic oscillators for two particles of masses m and M, frequencies ω and Ω, coupled by a potential cxy, c being a coupling constant. Notionally we think of x, m and ω applying to electronic motion and y, M and Ω to nuclear motion. We expect $m \ll M$, and $\omega \gg \Omega$, but do not use these inequalities in the development.

It is easily seen that Eq. (2.1) can be solved exactly by a rotation of axes by $\Theta = \frac{1}{2}\tan^{-1}(2c/(M\Omega^2 - m\omega^2))$. However for later comparison with the BO method it is better to treat the final term as a perturbation on solutions for the first four terms. These are products of simple harmonic oscillators. We denote by $|n, v\rangle$ product functions for the nth state of the oscillator representing electronic motion, and the vth state of nuclear motion.

The energy of the ground state including second-order coupling to $|1, 1\rangle$ is given by

$$\frac{1}{2}\hbar\omega + \frac{1}{2}\hbar\Omega - \frac{c^2\hbar}{4m\omega M\Omega}\left(\frac{1}{\omega + \Omega}\right). \tag{2.2}$$

Adiabatic approximation

The result (2.2) will now be compared with that from the adiabatic approximation with non-adiabatic corrections. The electronic Hamiltonian is

$$H_e = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 + cxy + \frac{1}{2}M\Omega^2 y^2, \tag{2.3}$$

y being treated as a parameter. The term linear in x can be removed by a shift of origin,

$$x' = x + \frac{cy}{m\omega^2}. \tag{2.4}$$

The eigenvalues of H_e are then found to be

$$\left(n + \frac{1}{2}\right)\hbar\omega - \frac{c^2 y^2}{2m\omega^2} + \frac{1}{2}M\Omega^2 y^2. \tag{2.5}$$

According to the adiabatic approximation this expression becomes the potential determining the y-motion, through

$$H = \left(n + \frac{1}{2}\right)\hbar\omega + \frac{p_y^2}{2M} + \frac{1}{2}M\Omega^2\left(1 - \frac{c^2}{mM\omega^2\Omega^2}\right)y^2, \tag{2.6}$$

with eigenvalues

$$E_{n,v} = \left(n + \frac{1}{2}\right)\hbar\omega + \left(v + \frac{1}{2}\right)\left(1 - \frac{c^2}{mM\omega^2\Omega^2}\right)^{1/2}\hbar\Omega. \tag{2.7}$$

The ground state energy, to order c^2, is

$$\frac{1}{2}\hbar\omega + \frac{1}{2}\hbar\Omega - \frac{c^2\hbar}{4mM\omega^2\Omega}. \tag{2.8}$$

This adiabatic value approaches the result (2.2) from the complete Hamiltonian for the nuclear frequency Ω very much smaller than the electronic frequency ω.

Note that, if $k = m\omega^2$ and $K = M\Omega^2$ are the respective force constants, then $(\Omega/\omega)^2 = (K/k)(m/M)$, illustrating the importance of both the masses and the potentials.

Non-adiabatic corrections

Expression (2.8) can be brought into precise agreement with the result (2.2) by making the non-adiabatic corrections. Following the usual development [3] the diagonal energy correction is given by

$$-\frac{\hbar^2}{2M}\int \chi_{00}(y)\int \phi^{(0)}(x,y)\frac{\partial^2}{\partial y^2}\phi^{(0)}(x,y)\,\mathrm{d}x\chi_{00}(y)\,\mathrm{d}y. \tag{2.9}$$

Using expression (2.5) we find for the diagonal correction

$$\frac{c^2\hbar}{4mM\omega^3}. \tag{2.10}$$

The off-diagonal ("momentum–momentum") matrix element joins $|0;0\rangle$ to $|1;1\rangle$, where we use the notation with semicolon, $|n;v\rangle \equiv \phi^{(n)}(x,y)\chi_{nv}(y)$,

$$-\frac{\hbar^2}{M}\int \chi_{11}(y)\int \phi^{(1)}(x,y)\frac{\partial}{\partial y}\phi^{(0)}(x,y)\,\mathrm{d}x\frac{\partial}{\partial y}\chi_{00}(y)\,\mathrm{d}y, \tag{2.11}$$

with a second order energy shift of $|0;0\rangle$ equal to

$$-\frac{c^2\hbar}{4mM}\frac{\Omega}{\omega^3(\omega+\Omega)} \tag{2.12}$$

leading to a total ground state energy in adiabatic approximation with non-adiabatic corrections equal to the result (2.2) from the complete Hamiltonian, both taken to order c^2.

First excited state

Anticipating discussion of the vibrational transition moment $|0,1\rangle \leftarrow |0,0\rangle$ we calculate the energy of the first excited vibrational level of the lowest electronic state. For the complete Hamiltonian, with perturbation theory applied to eigenfunctions of the first four terms of Eq. (2.1) we note that $|0,1\rangle$ is coupled to $|1,0\rangle$ and $|1,2\rangle$. The total energy of $|0,1\rangle$, corrected to order c^2, is given by

$$\frac{1}{2}\hbar\omega + \frac{3}{2}\hbar\Omega - \frac{c^2\hbar}{4mM\omega\Omega}\left\{\frac{1}{\omega-\Omega} + \frac{2}{\omega+\Omega}\right\}. \tag{2.13}$$

In adiabatic approximation the energy of $|0;1\rangle$ is

$$\frac{1}{2}\hbar\omega + \frac{3}{2}\hbar\Omega\left(1 - \frac{c^2}{2mM\omega^2\Omega^2}\right)^{1/2}. \tag{2.14}$$

The diagonal correction is the same as for the ground state, given in expression (2.10). The off-diagonal corrections result from the coupling to $|1;0\rangle$ and $|1;2\rangle$. Their sum, to c^2, is

$$-\frac{c^2\hbar\Omega}{4mM\omega^3}\left(\frac{1}{\omega-\Omega}+\frac{2}{\omega+\Omega}\right) \tag{2.15}$$

giving, with expressions (2.14) and (2.10) a total equal to expression (2.13) found from the complete Hamiltonian (2.1) up to terms in c^2.

3 Vibrational transition moment for bilinearly coupled oscillators

The moment for $|0,1\rangle \leftarrow |0,0\rangle$ in the method based on the complete Hamiltonian (2.1) without the Born–Oppenheimer approximation is found in a straightforward way. We need the matrix element of the total electric dipole moment $-e(x-y)$ connecting the perturbed initial and final states.

In order to get the moment correct to terms in c^2, we need perturbed wave functions as follows,

$$|0,0\rangle' = N_g\{|0,0\rangle + \lambda_{11}^{(1)}|1,1\rangle + \lambda_{02}^{(2)}|0,2\rangle\}, \tag{3.1}$$

where the prime refers to the perturbed wave function.
and

$$\lambda_{11}^{(1)} = -c\left(\frac{1}{2m\omega}\right)^{1/2}\left(\frac{1}{2M\Omega}\right)^{1/2}\left(\frac{1}{\omega+\Omega}\right), \tag{3.2}$$

$$\lambda_{02}^{(2)} = \sqrt{2}c^2\left(\frac{1}{2m\omega}\right)\left(\frac{1}{2M\Omega}\right)\frac{1}{2\Omega(\omega+\Omega)}. \tag{3.3}$$

For the excited state

$$|0,1\rangle' = N_e\{|0,1\rangle + \mu_{10}^{(1)}|1,0\rangle + \mu_{12}^{(1)}|1,2\rangle\}, \tag{3.4}$$

where

$$\mu_{10}^{(1)} = -c\left(\frac{1}{2m\omega}\right)^{1/2}\left(\frac{1}{2M\Omega}\right)^{1/2}\left(\frac{1}{\omega-\Omega}\right), \tag{3.5}$$

$$\mu_{12}^{(1)} = -\sqrt{2}c\left(\frac{1}{2m\omega}\right)^{1/2}\left(\frac{1}{2M\Omega}\right)^{1/2}\left(\frac{1}{\omega+\Omega}\right). \tag{3.6}$$

It is not necessary to include terms in c^2 in $|0,1\rangle'$: their contribution to the transition moment appears only in higher order.

The transition moment joining Eqs. (3.1) and (3.4) has contributions by electrons (from $|1,0\rangle \leftarrow |0,0\rangle$ and $|1,2\rangle \leftarrow |0,2\rangle$) as well as by nuclei. The expression for the transition moment is readily found to be

$$-eN_gN_e\left(\frac{\hbar}{2M\Omega}\right)^{1/2}\left\{1+\frac{c}{2m\omega}\left(\frac{2\omega}{\omega^2-\Omega^2}\right)\right. \\ \left.+\frac{c^2}{4mM\omega\Omega}\left(\frac{1}{(\omega+\Omega)}\right)\frac{\omega^2+3\omega\Omega-2\Omega^2}{\Omega(\omega^2-\Omega^2)}\right\}. \tag{3.7}$$

After evaluation of N_g and N_e the result is

$$e\left(\frac{\hbar}{2M\Omega}\right)^{1/2}\left\{1+\frac{c}{m(\omega^2-\Omega^2)}+\frac{c^2}{4mM\Omega^2}\frac{(\omega^2-3\Omega^2)}{(\omega+\Omega)^2(\omega-\Omega)^2}\right\}. \tag{3.8}$$

In Born–Oppenheimer approximation we begin with ground and excited state wave functions, including the non-adiabatic corrections. To get the transition moment correct to c^2 we need the first- and second-order corrections from the momentum–momentum coupling expression (2.11). For the ground state

$$|0;0\rangle' = n_g\{|0;0\rangle + \alpha_{11}^{(1)}|1;1\rangle + \alpha_{02}^{(2)}|0;2\rangle\}, \tag{3.9}$$

where

$$\alpha_{11}^{(1)} = \frac{c}{2(mM)^{1/2}}\left(\frac{\Omega}{\omega^3}\right)^{1/2}\frac{1}{\omega+\Omega}, \tag{3.10}$$

$$\alpha_{02}^{(2)} = \frac{\sqrt{2}c^2}{8mM}\left(\frac{1}{\omega^3}\right)\left(\frac{1}{\omega+\Omega}\right). \tag{3.11}$$

Likewise for the excited state,

$$|0;1\rangle' = n_e\{|0;1\rangle + \beta_{10}^{(1)}|1;0\rangle + \beta_{12}^{(1)}|1;2\rangle\}, \tag{3.12}$$

where

$$\beta_{10}^{(1)} = -\frac{c}{2(mM)^{1/2}}\left(\frac{\Omega}{\omega^3}\right)^{1/2}\left(\frac{1}{\omega-\Omega}\right), \tag{3.13}$$

$$\beta_{12}^{(1)} = \frac{\sqrt{2}c}{2(mM)^{1/2}}\left(\frac{\Omega}{\omega^3}\right)^{1/2}\left(\frac{1}{\omega+\Omega}\right). \tag{3.14}$$

Collecting terms, and using the modified frequency for y motion

$$\Omega' = \Omega(1 - c^2/mM\omega^2\Omega^2)^{1/2} \tag{3.15}$$

after a little algebra, we find that the transition moment joining Eq. (3.9) and (3.12) is equal, to terms in c^2, to expression (3.8).

Thus for bilinear coupling the energies of the states for the lowest vibrational transition, and the transition moment, are equal to terms quadratic in the coupling constant.

4 Energies of biquadratically coupled oscillators

Energies in second order perturbation theory

The Hamiltonian (1.11) for quadratic nuclear–electron coupling is

$$H = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2x^2 + \frac{p_y^2}{2M} + \frac{1}{2}M\Omega^2y^2 + \frac{1}{2}cm\omega^2x^2y^2. \tag{4.1}$$

In treating the complete Hamiltonian, without the Born–Oppenheimer approximation, we treat the last term as a perturbation on the eigenfunctions belonging to the first four terms as the unperturbed Hamiltonian. As before the eigenfunctions are products of harmonic oscillator wave functions belonging to x, m, ω and y, M, Ω, respectively.

With standard perturbation theory the total ground state energy, to terms in c^2,

$$\frac{1}{2}\hbar\omega + \frac{1}{2}\hbar\Omega + \frac{c\hbar^2\omega}{8M\Omega} - \frac{c^2\hbar^3\omega}{64M^2\Omega^2}\left(1 + \frac{\omega}{\Omega} + \frac{2\omega}{\omega + \Omega}\right). \tag{4.2}$$

A similar calculation applied to the state $|0, 1\rangle$, allowing for coupling to $|2, 1\rangle$, $|0, 3\rangle$ and $|2, 3\rangle$ gives

$$\frac{1}{2}\hbar\omega + \frac{3}{2}\hbar\Omega + \frac{3c\hbar^2\omega}{8M\Omega} - \frac{c^2\hbar^3\omega}{64M^2\Omega^2}\left(9 + \frac{3\omega}{\Omega} + \frac{6\omega}{\omega + \Omega}\right), \tag{4.3}$$

leading to the energy interval

$$E_{0,1} - E_{0,0} = \hbar\Omega + \frac{c\hbar^2\omega}{M\Omega} - \frac{c^2\hbar^3\omega}{64M^2\Omega^2}\left(8 + \frac{2\omega}{\Omega} + \frac{4\omega}{\omega + \Omega}\right). \tag{4.4}$$

Adiabatic approximation

In the adiabatic approximation we have from Eq. (4.1) the electronic Hamiltonian

$$H_e = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2(1 + cy^2) + \frac{1}{2}M\Omega^2 y^2, \tag{4.5}$$

where y is now a parameter. The energy levels of the electronic oscillator are

$$\left(n + \frac{1}{2}\right)\hbar\omega(1 + cy^2)^{1/2} \tag{4.6}$$

from which, following the usual development, the nuclear states are determined to terms in c^2 by

$$H = \frac{p_y^2}{2M} + \frac{1}{2}M\Omega^2\left(1 + \frac{\hbar\omega c}{2M\Omega^2}\right)y^2 - \frac{1}{16}\hbar\omega c^2 y^4 + \left(n + \frac{1}{2}\right)\hbar\omega. \tag{4.7}$$

We now treat the third term of Eq. (4.7) as a perturbation. The unperturbed solutions are for an oscillator of frequency $\Omega(1 + \hbar\omega c/2M\Omega^2)^{1/2}$ so that including the perturbation correction the ground state energy to terms in c^2 is

$$\frac{1}{2}\hbar\omega + \frac{1}{2}\hbar\Omega + \frac{\hbar^2\omega c}{8M\Omega} - \frac{c^2\hbar^3\omega}{64M^2\Omega^2}\left(3 + \frac{\omega}{\Omega}\right), \tag{4.8}$$

which expression (4.4) approaches for $\Omega \ll \omega$.

Non-adiabatic corrections

To take account of the non-adiabatic corrections we must broaden the discussion from the bilinear case. Here the "kinetic" coupling to the ground state

$$-\frac{\hbar^2}{2M}\int \chi_{nm}(y)\int \phi^{(n)}(x,y)\frac{\partial^2}{\partial y^2}\phi^{(0)}(x,y)\,\mathrm{d}x\chi_{00}(y)\,\mathrm{d}y \tag{4.9}$$

has, in addition to c^2-dependent diagonal term $n = m = 0$, off-diagonal terms that are linear and quadratic in c. The off-diagonal quadratic term is not needed for the energy calculation but enters the calculation of the transition moment, discussed later.

For the diagonal term, with use of

$$\phi^0(x,y) = (\beta/\pi)^{1/4}e^{-\beta x^2/2};\quad \beta = \frac{m\omega(1+cy^2)^{1/2}}{\hbar}, \tag{4.10}$$

we get for the x-integral of expression (4.9)

$$\frac{\hbar^2}{8M}\left(\frac{\partial\beta}{\partial y}\right)^2\frac{1}{8\beta^2} = \frac{c^2\hbar^2y^2}{16M} \tag{4.11}$$

up to terms in c^2. Completing the y-integration we find for the diagonal correction

$$\frac{c^2\hbar^3}{32M^2\Omega}. \tag{4.12}$$

The off-diagonal term, linear in c, couples the ground state $|0;0\rangle$ to $|2;0\rangle$.

$$-\frac{\hbar^2}{2M}\int \chi_{20}(y)\int \phi^{(2)}(x,y)\frac{\partial^2}{\partial y^2}\phi^{(0)}(x,y)\,\mathrm{d}x\chi_{00}(y)\,\mathrm{d}y = \frac{\hbar^2c}{4\sqrt{2}M} \tag{4.13}$$

The states $|0;0\rangle$ and $|2;0\rangle$ are also joined by the momentum–momentum coupling. The contribution is equal and opposite to Eq. (4.13), thus cancelling the "kinetic" coupling contribution.

The momentum–momentum coupling also connects the ground state to $|2;2\rangle$ the corresponding second-order energy correction being

$$-\frac{c^2\hbar^3}{32M^2}\frac{1}{(\omega+\Omega)}. \tag{4.14}$$

The sum of expressions (4.8), (4.12) and (4.14) gives a result for the ground state energy equal, to c^2, to expression (4.2) found in the calculation based on the complete Hamiltonian.

In the same way it is found that the energy of the state $|0;1\rangle$ and the lowest vibrational interval, are the same in the adiabatic approximation with non-adiabatic correcting terms.

5 Vibrational transition moment for biquadratically coupled oscillators

For comparison of the transition moment for $|0,1\rangle \leftarrow |0,0\rangle$ we need perturbed wave functions correct to c^2. In addition in order to get a transition moment containing all terms in c^2 we must include the second-order contribution by $|0, 2\rangle$ as well as its first-order term. The intermediate states are $|2, 0\rangle$, $|2, 2\rangle$, $|0, 0\rangle$ and $|0, 2\rangle$, the latter two being initial and final states, acting as intermediate states. The perturbed ground state is

$$\begin{aligned}|0, 0\rangle' = N_g \Big\{ &|0, 0\rangle - \frac{c\hbar}{8\sqrt{2}M}\left(\frac{\omega}{\Omega}\right)\frac{1}{\omega}|2, 0\rangle - \frac{c\hbar}{8\sqrt{2}M}\left(\frac{\omega}{\Omega}\right)\frac{1}{\Omega}|0, 2\rangle \\ &- \frac{c\hbar}{8M}\left(\frac{\omega}{\Omega}\right)\left(\frac{1}{\omega+\Omega}\right)|2, 2\rangle + \left(\frac{c\hbar}{8M}\right)^2\left(\frac{\omega}{\Omega}\right)^2 \\ &\times\left(\frac{1}{\sqrt{2}\Omega}\right)\left(\frac{1}{\omega} + \frac{5}{\omega+\Omega} + \frac{2}{\Omega}\right)|0, 2\rangle\Big\}. \end{aligned} \tag{5.1}$$

For the excited state

$$\begin{aligned}|0, 1\rangle' = N_e \Big\{ &|0, 1\rangle - \frac{3c\hbar}{8\sqrt{2}M}\left(\frac{\omega}{\Omega}\right)\frac{1}{\omega}|2, 1\rangle \\ &- \frac{\sqrt{3}c\hbar}{8\sqrt{2}M}\left(\frac{\omega}{\Omega}\right)\frac{1}{\Omega}|0, 3\rangle - \frac{\sqrt{3}c\hbar}{8M}\left(\frac{\omega}{\Omega}\right)\left(\frac{1}{\omega+\Omega}\right)|2, 3\rangle\Big\}. \end{aligned} \tag{5.2}$$

In the perturbed wave functions (5.1) and (5.2), only those second-order terms that can give non-zero contributions to the moment have been included. The transition moment includes terms from the nuclear motion only. After including the terms to c^2 in the expansion of the normalizers N_g and N_e it is given by

$$\begin{aligned}e\langle 1, 0|y|0, 0\rangle' = e\left(\frac{\hbar}{2M\Omega}\right)^{1/2}\Big(1 &- \left(\frac{c\hbar}{8M}\right)\left(\frac{\omega}{\Omega}\right)\frac{1}{\Omega} \\ &+ \left(\frac{c\hbar}{8M}\right)^2\left(\frac{\omega}{\Omega}\right)^2\Big\{\frac{1}{\omega\Omega} + \frac{5}{\Omega(\omega+\Omega)} + \frac{5}{2\Omega^2} \\ &- \frac{1}{\omega^2} + \frac{3}{\omega(\omega+\Omega)} + \frac{1}{(\omega+\Omega)^2}\Big\}\Big). \end{aligned} \tag{5.3}$$

In the Born–Oppenheimer approximation there is again no electronic component in the moment. The perturbed ground state, denoted by $|0; 0\rangle'$ has a correction due to coupling to $|0; 2\rangle$ by the perturbation due to the y^4 potential term given in expression (4.7). There is a second coupling to $|0; 2\rangle$ through the off-diagonal part of the kinetic energy given in Eq. (4.13).

Both the kinetic energy and momentum–momentum terms couple $|0; 0\rangle$ to $|2; 0\rangle$; these contributions exactly cancel. There is also a momentum coupling to $|2; 2\rangle$. The corrected perturbed ground state is given in Eq. (5.4), including all terms giving contributions to the transition moment up to order c^2.

$$\begin{aligned}|0; 0\rangle' = N_g\Big\{ &|0; 0\rangle + \left(\frac{c\hbar}{8M}\right)^2\left(\frac{\omega}{\Omega}\right)\frac{\Omega}{\omega(\omega+\Omega)}|2; 2\rangle \\ &+ 3\sqrt{2}\left(\frac{c\hbar}{8M}\right)^2\left(\frac{\omega}{\Omega}\right)^2\frac{1}{\omega\Omega}|0; 2\rangle \\ &- \sqrt{2}\left(\frac{c\hbar}{8M}\right)^2\left(\frac{\omega}{\Omega}\right)^2\frac{1}{\omega^2}|0; 2\rangle\Big\}. \end{aligned} \tag{5.4}$$

In the excited state the coefficients of $|2; 1\rangle$ similarly cancel. We have

$$|0; 1\rangle' = N_e\left\{|0; 1\rangle + \sqrt{3}\left(\frac{c\hbar}{8M}\right)\left(\frac{\omega}{\Omega}\right)\frac{\Omega}{\omega(\omega+\Omega)}|2; 3\rangle\right\}. \tag{5.5}$$

Now, taking account of the altered nuclear frequency $\Omega(1 + \hbar\omega c/2M\Omega^2)^{1/2}$ and of terms to c^2 in the normalizers, we find for the Born–Oppenheimer transition moment, for comparison with Eq. (5.3),

$$e\langle 1; 0|y|0; 0\rangle' = e\left(\frac{\hbar}{2M\Omega}\right)^{1/2}\left\{1 - \frac{c\hbar\omega}{8M\Omega^2} + \left(\frac{c\hbar^2}{8M}\right)^2\left(\frac{\omega}{\Omega}\right)^2 \times\left(\frac{5}{2\Omega^2} + \frac{6}{\omega\Omega} + \frac{\Omega^2}{\omega^2(\omega+\Omega)^2} - \frac{2}{\omega^2}\right)\right\}. \tag{5.6}$$

It is readily shown that Eqs. (5.3) and (5.6) are identical, both reducible to

$$e\left(\frac{\hbar}{2M\Omega}\right)^{1/2}\left\{1 - \frac{c\hbar\omega}{8M\Omega^2} + \left(\frac{c\hbar}{8M}\right)^2\left(\frac{\omega}{\Omega}\right)^2 \times\left\{\frac{5}{2\Omega^2} + \frac{6\omega^3 + 10\omega^2\Omega + 2\omega\Omega^2 - \Omega^3}{\Omega\omega^2(\omega+\Omega)^2}\right\}\right\}, \tag{5.7}$$

showing that the transition moment, in terms in c^2, is the same in the Born–Oppenheimer approximation, and according to the complete Hamiltonian.

6 The near-resonance ("curve crossing") limit

The adiabatic approximation fails in the case that a vibronic level belonging to one electronic state is nearly resonant with another pure electronic state, as in the close approach of two potential curves. The extent of improvements to the adiabatic approximation from non-adiabatic terms is not known.

In the coupled harmonic oscillator model we take two electronic states, with displacements x and y, frequencies ω_x and ω_y, and a vibration with displacement ξ and frequency Ω built on the x-state. $\omega_x + \Omega \approx \omega_y$. Occupation numbers in the oscillators x, y and ξ are denoted $|n_x, n_y; n_\xi\rangle$. The base states $|0, 1; 0\rangle$ and $|1, 0; 1\rangle$ are nearly in resonance.

In a calculation with the complete Hamiltonian, with linear coupling,

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2}m\omega_x^2x^2 + \frac{1}{2}m\omega_y^2y^2 + \frac{p_\xi^2}{2M} + \frac{1}{2}M\Omega^2\xi^2 + cxy\,\xi, \tag{6.1}$$

the base states are in first-order coupled to each other and to $|0, 1; 2\rangle$, $|2, 1; 0\rangle$, $|2, 1; 2\rangle$ and $|1, 2; 1\rangle$. Since the energy gaps between individual base states and others are much greater than the gap $\delta = \omega_x + \Omega - \omega_y$ between the near-resonant pair the corresponding off-resonance shifts are found by perturbation theory. The effect is a modified separation $\hbar\delta - \gamma$ between the perturbed $\langle 0, 1; 0\rangle'$ and $|1, 0; 1\rangle'$, where

$$\gamma = \frac{2c^2\Delta^2}{\hbar}\left(-\frac{1}{\omega_x - \Omega - \omega_y} + \frac{1}{\omega_x - \Omega + \omega_y} + \frac{1}{\omega_x + \Omega + \omega_y}\right) \tag{6.2}$$

and

$$\Delta^2 = \frac{\hbar^3}{8m^2 M \omega_x \omega_y \Omega}. \tag{6.3}$$

Noting that

$$\langle 1, 0; 1 | cxy\xi | 0, 1; 0 \rangle = c\Delta \tag{6.4}$$

and solving the 2×2 secular problem we have for the level splitting of the near resonant states with the complete Hamiltonian (6.1)

$$E_1 - E_2 = \{(\hbar\delta + \gamma)^2 + 4c^2\Delta^2\}^{1/2}. \tag{6.5}$$

In applying the BO approximation we take

$$H_e = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{1}{2} m\omega_x^2 x^2 + \frac{1}{2} m\omega_y^2 y^2 + \frac{1}{2} M\Omega^2 \xi^2 + cxy\xi. \tag{6.6}$$

After coupling the electronic states $|1, 0\rangle$ and $|0, 1\rangle$ to each other and to $|2, 1\rangle$ and $|1, 2\rangle$ respectively we find the splitting, in adiabatic approximation,

$$E_1^{ad} - E_2^{ad} = \hbar\delta - \frac{8c^2\Delta^2\omega_y}{\hbar(\omega_y^2 - \omega_x^2)} \tag{6.7}$$

For typical values near resonance (6.7) is between 1 and 2 orders of magnitude too small compared with Eq. (6.5).

Next, to include the non-adiabatic correction to Eq. (6.7) we use the corrected wave function (6.8), excluding a term in $|2, 1; 0\rangle$ which does not contribute to the end result,

$$|1, 0; 1\rangle' = |1, 0; 1\rangle - \frac{c\xi}{2m(\omega_y\omega_x)^{1/2}(\omega_y - \omega_x)} |0, 1; 1\rangle \tag{6.8}$$

and find for the momentum–momentum matrix element between $|1, 0; 1\rangle'$ and $|0, 1; 0\rangle$

$$c\Delta \frac{\Omega}{\omega_y - \omega_x}. \tag{6.9}$$

The 2×2 secular equation gives for the BO level splitting, to order c^2,

$$E_1^{\text{corr}} - E_2^{\text{corr}} = \left(\hbar^2\delta^2 - \frac{4c^2\Delta^2}{\omega_y - \omega_x} \left\{ \frac{4\omega_y\delta}{(\omega_y + \omega_x)} - \frac{\Omega^2}{\omega_y - \omega_x} \right\} \right)^{1/2}, \tag{6.10}$$

Eq. (6.10) cannot be brought into agreement algebraically with the complete Hamiltonian result (6.5). It is however easily shown that for physically reasonable values of ω_x, ω_y and Ω, chosen to be near to the resonance limit $\delta = 0$, Eq. (6.10) is very close to Eq. (6.5). The BO adiabatic approximation, with non-adiabatic corrections, gives an excellent result in this case also.

7 Intensity transfer in a forbidden electronic transition

The tests so far apply to cases in which corrections are applied to a large zeroth order result. The corrections provide the entire result in calculations of intensity stealing caused by vibronic interaction characteristic of many experimental spectra. The typical situation is one in which a forbidden electronic transition is made weakly allowed by vibrations which couple the forbidden electronic transition to an allowed transition from which the intensity can be said to be borrowed or stolen. The best known case is in the benzene 260 nm spectrum.

In the model system both electronic and nuclear motion are again harmonic oscillators. The lowest allowed electronic transition is $|1,0\rangle \leftarrow |0,0\rangle$, and the lowest forbidden $|2,0\rangle \leftarrow |0,0\rangle$. The forbidden vibronic transition to be considered is $|2,1\rangle \leftarrow |0,0\rangle$. Vibronic coupling mixes $|2,1\rangle$ with $|1,0\rangle$, with the result that the forbidden transition gains intensity by borrowing from the allowed $|1,0\rangle \leftarrow |0,0\rangle$. There is a second component from $|2,1\rangle \leftarrow |1,1\rangle$. The bilinear interaction is of dipole–dipole form, and so models real systems in which vibronic effects depend on the electric dipole moment created by nuclear displacement.

With use of the complete bilinear coupling Hamiltonian (2.1) we find for the ground and excited states

$$|0,0\rangle' = n_g\{|0,0\rangle + \lambda^{(1)}_{11}|1,1\rangle + \lambda^{(2)}_{20}|2,0\rangle + \lambda^{(2)}_{22}|2,2\rangle\}, \tag{7.1}$$

$$|2,1\rangle' = n_e\{|2,1\rangle + \mu^{(1)}_{10}|1,0\rangle + \mu^{(1)}_{12}|1,2\rangle + \mu^{(2)}_{01}|0,1\rangle\}. \tag{7.2}$$

The transition moment for $|2,1\rangle' \leftarrow |0,0\rangle'$ has terms linear in c borrowed from the allowed transitions $|1,0\rangle \leftarrow |0,0\rangle$ and $|2,1\rangle \leftarrow |1,1\rangle$. They are

$$-e\left(\frac{\hbar}{2m\omega}\right)^{1/2}\frac{\sqrt{2}c\chi}{\omega+\Omega} + e\sqrt{2}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\frac{c\chi}{\omega+\Omega} = 0, \tag{7.3}$$

where $-e(\hbar/2m\omega)^{1/2}$ is the electronic transition moment $|1,0\rangle \leftarrow |0,0\rangle$.

Contributions in c^2 represent borrowing from vibrational transitions. They are

$$\sqrt{2}ec^2\left(\frac{\hbar}{2M\Omega}\right)^{1/2}\chi^2\left\{\frac{1}{\omega(\omega-\Omega)} + \frac{1}{\omega(\omega+\Omega)} - \frac{2}{\omega^2-\Omega^2}\right\} = 0. \tag{7.4}$$

In Eq. (7.4) the quantity $e\sqrt{2}(\hbar/2M\Omega)^{1/2}$ is the transition moment for y (nuclear) transitions $|v,2\rangle \leftarrow |v;1\rangle$.

The vanishing of the y terms in Eq. (7.4) is not surprising, since a forbidden electronic transition is not expected to borrow vibrational intensity.

The result (7.3) needs a more critical appraisal. Representation of electronic states as states of a harmonic oscillator has some unsatisfactory features. The transition moment for the allowed transition $|2,1\rangle \leftarrow |1,1\rangle$ is $\sqrt{2}$ times that for $|1,0\rangle \leftarrow |0,0\rangle$. This relationship, coupled with the ratio of the coefficients $\lambda^{(1)}_{11}/\mu^{(1)}_{10}$ gives the cancellation in Eq. (7.3). However in real physical systems these relationships would not be expected. Also the energy differences $(E_{11} - E_{00})$ and $(E_{21} - E_{10})$ are equal in the harmonic oscillator model. In real systems they are unrelated. We should therefore write in place of Eq. (7.3) the expression for the borrowed electronic transition moment

$$\frac{\sqrt{2}c\chi}{E_{11}-E_{00}}\underset{\sim}{M}(|1,0\rangle \leftarrow |0,0\rangle) + \frac{c\chi}{E_{21}-E_{10}}\underset{\sim}{M}(|2,1\rangle \leftarrow |1,1\rangle) \tag{7.5}$$

in terms of the moments $\underset{\sim}{M}$ of the indicated transitions as the result for the transition moment for the complete Hamiltonian.

In the BO approach to the borrowed transition moment for $|2;1\rangle \leftarrow |0;0\rangle$ it is necessary to recall the results of Sect. 2, particularly the origin shift (2.5) to remove the term linear in x from the electronic Hamiltonian (2.4), and the modified frequency (3.16) for y motion.

The frequency of x motion is unaltered from its uncoupled value ω. Thus the state $|2;1\rangle$ refers to a two-quantum state of x-frequency ω, and a one-quantum state of y frequency Ω'.

The perturbed wave functions for ground and excited states bring in the same basis states as those for the complete Hamiltonian in Eqs. (7.1) and (7.2).

$$|0;0\rangle' = n_g\{|0;0\rangle + \lambda_{11}^{(1)}|1;1\rangle + \lambda_{20}^{(2)}|2;0\rangle + \lambda_{22}^{(2)}|2;2\rangle + \lambda_{20}^{(2)\prime}|2;0\rangle\}, \quad (7.6)$$

$$|2;1\rangle' = n_g\{|2;1\rangle + \mu_{10}^{(1)}|1;0\rangle + \mu_{01}^{(2)}|0;1\rangle + \mu_{01}^{(2)\prime}|0,1\rangle\}. \quad (7.7)$$

The primed coefficients refer to matrix elements of the kinetic energy.

If $\Omega' = \Omega$ it is found that all unprimed coefficients in Eqs. (7.6) and (7.7) are equal to (Ω/ω) times the corresponding terms for the complete Hamiltonian. Accordingly in the case where the allowed transitions are given harmonic oscillator transition moments for the linear and quadratic terms the borrowed intensity vanishes as in Eqs. (7.3) and (7.4).

Replacement of Ω by the corrected value Ω' does not affect these results to order c^2. The linear terms in the transition moment are quantities borrowed from electronically allowed transitions. As already noted they exactly cancel when harmonic oscillator moments are used. If the moments are treated as parameters as in the text leading to Eq. (7.5) we do not in general get a cancellation. If the moments are $\underset{\sim}{M}(|1,0\rangle \leftarrow |0,0\rangle)$ and $\underset{\sim}{M}(|2;1\rangle \leftarrow |1,1\rangle)$ we find for the borrowed moment

$$\frac{c\chi\Omega}{(\omega+\Omega)\omega}(\sqrt{2}\underset{\sim}{M}(|1,0\rangle \leftarrow |0,0\rangle + \underset{\sim}{M}(|2,1\rangle \leftarrow |1,1\rangle), \quad (7.8)$$

which is Ω/ω times the expression (7.5) for the complete Hamiltonian. Account may also be taken of different energy denominators for the two terms, as in expression (7.5). The two methods do not in this case agree.

Acknowledgement. We thank Dr. Gad Fischer for his comments on the text.

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