NEAR RESONANCE INTERACTIONS IN THE B-O SCHEME. 
THE VIBRONIC MECHANISM PERTINENT TO RADIATIONLESS TRANSITIONS 
AND INHOMOGENEOUS LINE BROADENING *

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Near resonance vibronic interactions in the Born-Oppenheimer approximation - pertinent to radiationless transitions and inhomogeneous line broadening - are shown to be independent of the relevant electronic energy separation and to be practically equivalent to those deduced in the crude adiabatic scheme. The present theoretical results agree with those previously deduced by the authors in alternative procedures. The superiority of the B-O approximation for resonant interactions of this type - which rests on the belief that the off-diagonal elements arising in this scheme are smaller than those resulting in alternative schemes and inversely proportional to the electronic energy separation - is therefore questionable.

The Born-Oppenheimer approximation [1] is thought by most authors to be advantageous to other possible procedures in computing molecular spectra, molecular structure and molecular processes. This view rests essentially on the belief that the off-diagonal elements arising in the B-O approximation are inversely proportional to the relevant electronic energy separation. Thus, it seems well established that for an electronic energy gap larger than a typical vibrational frequency, the resulting interactions are smaller than those arising in alternative schemes.

Here it is shown that this well-established concept is not generally valid. Near resonance interactions in the B-O scheme are claimed to be independent of the relevant electronic energy separation and to be practically equivalent (and not smaller) to those arising in the crude adiabatic scheme.

The phenomena of electronic radiationless transitions and inhomogeneous line broadening in large molecules are closely related. The recent theoretical formulation of these phenomena [2-4] have used the Born-Oppenheimer approximate wavefunctions and have concluded that the relevant parameter in both cases is the matrix element of the nuclear kinetic energy operator between two BO states. Recently it was argued [5, 6] that (for line broadening) one may use the "crude adiabatic" [7] functions instead. The relevant parameter is then the matrix element of the difference in the potential term between its value at any nuclear position and its value at some standard position (usually the equilibrium position of the ground state). Using this [5], we found line widths two orders of magnitude larger than those found using the BO matrix element when that matrix element was approximated using a standard approximation. We pointed out that this approximation (using the Herzberg Teller electronic function instead of the true BO function) can be seriously in error. In the present note, we present an alternative calculation of this matrix element. In the present case, we show that the BO matrix element is approximately equal to the crude adiabatic in the case of the two vibronic states being degenerate, and that it is equal to the standard Herzberg Teller value when the two vibronic states are those normally used when discussing the Herzberg Teller effect (the ground vibronic level of one electronic state and the first vibrationally excited level of a second electronic state). We feel that this partially resolves the discrepancy between the two approaches.

The calculation goes as follows: we consider a simple model system of two electronic states in the crude adiabatic representation. We assume a simple form for the off-diagonal matrix elements and calculate the exact BO states for this model. Then we calculate the matrix element of the nuclear kinetic energy operator in the BO basis and compare it to the relevant matrix element in the crude adiabatic
The model is as follows: consider two electronic wavefunctions, eigensolutions to \( H_e(q, Q_0) = T(q) + U(q, Q_0) \):

\[
H_e(q, Q_0) \phi^C_i(q, Q_0) = E^C_i \phi^C_i(q, Q_0). \tag{1}
\]

Then the crude adiabatic vibronic wavefunctions are written as:

\[
\psi^C_{\lambda \lambda}(q, Q) = \phi^C_i(q, Q_0) \chi^C_{\lambda \lambda}(Q),
\]

where

\[
[T(q) + \phi^C_i(q, Q_0)\big| T(q) + U(q, Q) \big| \phi^C_i(q, Q_0)] \chi^C_{\lambda \lambda}(Q) = \varepsilon^C_{\lambda \lambda} \chi^C_{\lambda \lambda}(Q).
\]

We shall assume that the off diagonal matrix element of the total hamiltonian between the two electronic states is given by

\[
\langle \phi^C_i(q, Q_0) | H | \phi^C_j(q, Q_0) \rangle = \frac{\gamma Q K}{a(Q) \phi^C_k(i, j) + a(Q) \phi^C_j(i, j)} = \gamma Q_k,
\]

where \( Q_k \) is the promoting mode coordinate. The relevant matrix element in the theory of line broadening is then:

\[
\lambda^C = \gamma \langle \chi^C_{1,1} | Q_k | \chi^C_{2,2} \rangle Q.
\]

We now calculate the BO electronic states for this model. This requires diagonalizing \( H_e(q, Q) \). The \( H_e \) matrix in the crude representation is given as

\[
H_e(q, Q) = \begin{pmatrix} E^C_1(q) & \gamma Q_k \\ \gamma Q_k & E^C_2(q) \end{pmatrix},
\]

where \( E^C_i(q) = \langle \phi^C_i(q, Q_0) | H | \phi^C_i(q, Q_0) \rangle \). Diagonalizing \( H_e \), we find the electronic eigenfunctions and eigenvalues (nuclear potentials) to be

\[
E^C_{\pm}(Q) = \frac{1}{2}(E^C_1 + E^C_2) \pm \frac{1}{2}(E^C_1 - E^C_2) + \gamma^2 Q_k^2 \frac{1}{2},
\]

\[
\phi^a_i(q, Q) = a(Q)\phi^C_i + b(Q)\phi^C_j; \quad \phi^b_i(q, Q) = -b(Q)\phi^C_i + a(Q)\phi^C_j,
\]

where

\[
a(Q) = 2^{-1/2} \left[ 1 + \left( 1 - 4\gamma^2 Q_k^2 / \left( E^C_1 - E^C_2 \right) \right)^{1/2} \right], \quad b(Q) = \gamma Q_k / [a(Q) (E^C_1 - E^C_2)].
\]

Notice that in this model, the two BO energy values cannot be degenerate unless \( Q_k = 0 \) and \( E^C_1 = E^C_2 \) for some value of \( Q_k, k \neq i \).

The matrix element for line broadening is

\[
\lambda^a = \langle \phi^a_i(q, Q) \chi^a_{\lambda \lambda}(Q) | T(q) | \phi^a_j(q, Q) \chi^a_{\mu \mu}(Q) \rangle Q, \tag{8}
\]

where the \( \chi^a_{\lambda \lambda} \) are eigenfunctions of \( T(q) + E^a_\pm(q) \) with eigenvalues \( a \mp \lambda \). We can write (8) as

* The molecular hamiltonian - \( H(q, Q) \) - is displayed in the usual way; \( H(q, Q) = T(q) + U(q, Q) + H(q) \), whereas \( T(q) \) and \( T(Q) \) denote the kinetic energy operators of the electrons and nuclei respectively, whereas \( U(q, Q) \) designates the molecular potential and \( Q_0 \) is the ground state equilibrium configuration.
Using the fact that
\[ T = \frac{1}{2} \sum \frac{\partial^2}{\partial Q_i \partial Q_j} = \frac{i}{2} \frac{\partial}{\partial Q} \frac{\partial}{\partial Q} \]
and the fact that \( \chi_{\pm \lambda}^a(Q) \) are eigenfunctions of \( T(Q) + E_a^\pm(Q) \), we find,

\[ \lambda^a = \langle \chi_{\pm \lambda}^a(Q) | b T a | \chi_{- \mu}^a(Q) \rangle - \langle \chi_{- \mu}^a(Q) | b T a | \chi_{\pm \lambda}^a(Q) \rangle \]

or:

\[ \lambda^a = \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle + \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle - \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle + \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle \]

where, the Herzberg-Teller type adiabatic wavefunctions adopted by previous authors [2-4] are

\[ \phi_\pm^a(q, Q) = \frac{\gamma Q_k}{E_\pm(Q) - E_\mp(Q)} \phi_\pm \]

Evaluating the \( T(Q) \) matrix elements arising through the first order procedure [eq. (12)] we get:

\[ \lambda^a = \langle \chi_{\pm \lambda}^a | [T(Q) + E_a^\pm(Q)] \gamma Q_k | \chi_{- \mu}^a \rangle \]

or:

\[ \lambda^a = \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle - \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle + \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle - \langle \chi_{\pm \lambda}^a \gamma Q_k \chi_{- \mu}^a \rangle \]

Now, from the definition of \( a(Q) \) we can conclude that the maximum value of \( a \) is 1 and the minimum value is 2-1/2 (and that only if \( E_a^1 = E_a^2 \) at \( Q = 0 \) which is rarely the case for the systems under consideration). In most cases \( a \) will vary very little and a detailed analysis of \( bda(Q)/dQ \) shows that the quantity varies as \( (E_a^1 - E_a^2)^{-1} \). Hence, we feel that the sum of the terms involving this quantity will be negligible. Considering why the standard procedure [2-4], adopting Herzberg-Teller type B-O wavefunctions fails to give the same result, we note that the B-O (adiabatic) wavefunctions to first order are:

\[ \phi_\pm^a(q, Q) \approx \frac{\gamma Q_k}{E_\pm(Q) - E_\mp(Q)} \phi_\pm \]

whereas, the Herzberg-Teller type adiabatic wavefunctions adopted by previous authors [2-4] are

\[ \phi_\pm^a(q, Q) = \frac{\gamma Q_k}{E_\pm(Q) - E_\mp(Q)} \phi_\pm \]

where \( \phi_\pm \) are the adiabatic wavefunctions of the system under consideration.
equal to the result in eq. (11) with the approximations mentioned there. Thus, in these approximations we find that near resonance interactions in the B-O scheme (i.e. when $\epsilon_{+\lambda}^{a} \approx \epsilon_{-\mu}^{a}$) are given by:

$$\lambda^{a} = \gamma \langle \chi_{+\lambda}^{a} | Q_{k} | \chi_{-\mu}^{a} \rangle \approx \lambda^{c},$$

whereas, in the case where $\epsilon_{+\lambda}^{a} - \epsilon_{-\mu}^{a} \approx \omega_{k}^{a} (Q_{0}^{a} - Q_{0}^{b})$ the results are very different. For example, when $\epsilon_{+\lambda}^{a} - \epsilon_{-\mu}^{a} = E_{+}^{a} (Q_{0}^{a}) - E_{-}^{a} (Q_{0}^{b}) - \omega_{k}$ (the Herzberg-Teller case), we find that:

$$\lambda^{a} \approx \frac{\gamma \omega_{k}^{a}}{E_{+}^{a} (Q_{0}^{a}) - E_{-}^{a} (Q_{0}^{b})} \langle \chi_{+\lambda}^{a} | Q_{k} | \chi_{-\mu}^{a} \rangle.$$

Finally we note that for $\epsilon_{+\lambda}^{a} < \epsilon_{-\mu}^{a}$, $\lambda^{a} > \lambda^{c}$. Proceeding in the standard procedure [2-4], one gets that the $T(Q)$ matrix elements are invariantly given by eq. (16). However, as shown by us [5] near-resonance interactions in the Herzberg-Teller scheme with respect to the total molecular hamiltonian are still equivalent to those deduced in the crude adiabatic scheme, or in the proper approximate B-C procedure presented above. In conclusion, we have derived the vibronic mechanism pertinent to inhomogeneous line broadening and electronic relaxation processes in the Born-Copenhagen approximation. Moreover, in contradiction to the accepted idea, we have shown that near resonance interactions arising in the B-O scheme are not dependent on the relevant electronic energy (except in the Franck-Condon factors, of course) separation and are no: smaller and are practically equivalent to those resulting in the crude adiabatic scheme or in the Herzberg-Teller procedure. The superiority of the B-O approximation for these resonant interactions is thus questionable.

* The integral $\langle \chi_{+\lambda}^{a} | \left[ \frac{1}{E_{+}^{a} (Q_{0}^{a}) - E_{-}^{a} (Q_{0}^{b})} \right] \chi_{-\mu}^{a} \rangle$ was integrated analytically for one mode when the two potentials $E_{\pm}^{a} (Q)$ differ in the force constants to give $\langle \chi_{+\lambda}^{a} | \left[ \frac{1}{E_{+}^{a} (Q_{0}^{a}) - E_{-}^{a} (Q_{0}^{b})} \right] \chi_{-\mu}^{a} \rangle$.

REFERENCES


