

Properties of nonadiabatic couplings and the generalized Born–Oppenheimer approximation

Brian K. Kendrick^{a,*}, C. Alden Mead^{b,1}, Donald G. Truhlar^{c,2}

^a *Theoretical Division (T-12, MS-B268), Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

^b *92 Bartram Road, Savannah, GA 31411, USA*

^c *Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, MN 55455, USA*

Received 13 June 2001; in final form 5 December 2001

Abstract

We present a new analysis of the nonadiabatic coupling terms in the coupled equations for nuclear motion wave functions when the Born–Oppenheimer (BO) representation is used for the electronic wave function. The new analysis leads to a criterion for truncating the series and neglecting terms in the coupled equations of motion. We show that in general the nonremovable part of the coupling is of the same magnitude as the removable part, except near intersections of the adiabatic states. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The Born–Oppenheimer (BO) separation of electronic and nuclear motion (various formulations are discussed in many places [1–4]) is fundamental to the quantum theory of molecules. The success of this approach depends on the smallness of the electronic-to-nuclear mass ratio, $(1/M)$, in atomic units where the electronic mass is unity. The original paper by Born and Oppenheimer [5] established the leading terms of asymptotic series

in powers of $\kappa = (1/M)^{1/4}$ for molecular wave functions, energies, and other quantities of interest. To lowest order in κ , the molecular wave function is expressible as a product of an electronic and a nuclear part

$$\Psi(r, R) = \psi(R)\varphi(r, R), \quad (1)$$

where r and R are electronic and nuclear coordinates respectively, $\psi(R)$ describes the nuclear motion and $\varphi(r, R)$ is an eigenfunction of the electronic Hamiltonian with the nuclei fixed at R . It thus depends parametrically on R . Since the time of Born and Oppenheimer, the method has been extended and generalized in various ways, but has remained the basis of most applications of quantum mechanics to molecules.

It is also well known that there are many cases in which the simple form (1) does not suffice, and one needs to consider two or more electronic states

* Corresponding author. Fax: +1-505-665-3909.

E-mail addresses: bkendric@lanl.gov (B.K. Kendrick), cmead@sprintmail.com (C. Alden Mead), truhlar@umn.edu (D.G. Truhlar).

¹ Fax: +912-598-1899.

² Fax: +612-626-9390.

for a good approximation. For example, one requires more than one electronic state to apply quantum mechanics to electronic-to-vibrational energy transfer and photochemistry induced by ultraviolet light. Furthermore, for any kind of application, the simple form (1) breaks down if two or more electronic states become degenerate, or nearly so, for regions of interest in the R -space. There is also the phenomenon of the geometric phase, in which (1) suffices for a good description, but $\varphi(r, R)$ is not single-valued in R (if taken to be real and a smooth function of R) because of a conical intersection of two electronic energy surfaces in some manifold (not necessarily that of direct interest for the problem considered) of R -space [6–11].

The plan of the paper is as follows. Section 2 presents an analysis of the coupling terms in the coupled equations that one obtains when using a BO adiabatic basis, and this analysis leads to criteria for truncating the series. Section 3 examines the consequences of the analysis for coupled equations in other representations that may be obtained by orthogonal transformations of the adiabatic basis. Section 4 discusses approximations to the coupled equations. Section 5 discusses the geometric phase approach. Section 6 contains concluding remarks.

2. Decoupling the adiabatic representation

We use atomic units, in which electronic mass and charge are unity, and the unit of length is the Bohr. The Schrödinger equation satisfied by the molecular wave function for a molecule with N nuclei is

$$\left[-\frac{1}{2M}\nabla^2 + \hat{H}_{\text{el}}(R) \right] \Psi(r, R) = E\Psi(r, R), \quad (2)$$

where the first term contains a $3N$ -dimensional Laplacian, with nuclear coordinates mass-scaled as necessary, and $\hat{H}_{\text{el}}(R)$ is the familiar electronic Hamiltonian, an operator in the electronic space that depends parametrically on R . Let r denote the electronic coordinates. In the BO approach, one expands $\Psi(r, R)$ in eigenfunctions of $\hat{H}_{\text{el}}(R)$

$$\Psi(r, R) = \sum_{j=1}^{\infty} \psi_j(R) \varphi_j(r, R), \quad (3)$$

where the $\varphi_j(r, R)$ satisfy the eigenvalue equation

$$\hat{H}_{\text{el}}(R) \varphi_j(r, R) = V_j(R) \varphi_j(r, R), \quad (4)$$

and the normalization condition

$$\langle j(R) | k(R) \rangle \equiv \int \varphi_j^*(r, R) \varphi_k(r, R) dr = \delta_{jk}. \quad (5)$$

The representation (3) with the condition (4) is called the adiabatic representation. Inserting (3)–(5) into (2), we obtain coupled equations for the ψ_j

$$\begin{aligned} & -\frac{1}{2M}\nabla^2 \psi_j + V_j(R) \psi_j - \frac{1}{M} \sum_{k=1}^{\infty} \vec{F}_{jk} \cdot \nabla \psi_k \\ & - \frac{1}{2M} \sum_{k=1}^{\infty} G_{jk} \psi_k = E \psi_j, \end{aligned} \quad (6)$$

where the gradient is $3N$ -dimensional,

$$\begin{aligned} \vec{F}_{jk}(R) &= \langle j(R) | \nabla k(R) \rangle \\ &\equiv \int \varphi_j^*(r, R) \nabla \varphi_k(r, R) dr, \end{aligned} \quad (7)$$

and

$$\begin{aligned} G_{jk}(R) &= \langle j(R) | \nabla^2 k(R) \rangle \\ &\equiv \int \varphi_j^*(r, R) \nabla^2 \varphi_k(r, R) dr. \end{aligned} \quad (8)$$

The nondiagonal terms involving \vec{F}_{jk} and G_{jk} are usually called nonadiabatic coupling terms.

It will be convenient to label the $3N$ nuclear coordinates as x_μ, x_ν, \dots , and to define the vector matrix $\vec{\mathbf{F}}$ with vector components $\mathbf{F}_\mu, \mathbf{F}_\nu$, etc. and matrix elements \vec{F}_{jk} , and similarly the scalar matrix \mathbf{G} with matrix elements G_{jk} .

The quantities \vec{F}_{jk} and G_{jk} describe the coupling between the different electronic states. They also describe the way in which the electronic eigenfunctions φ_j depend on the nuclear coordinates. Here we obtain a few useful properties of the coupling quantities; this leads us into a discussion of the permissibility of truncating the series (6) after a small number of terms, a topic incorrectly treated in a recent study [12].

By differentiating (5) and using the definitions (7) and (8), it is straightforward to obtain the following relations:

$$\vec{\mathbf{F}} + \vec{\mathbf{F}}^\dagger = 0, \quad (9)$$

$$\mathbf{G} + \mathbf{G}^\dagger - 2\vec{\mathbf{F}} \cdot \vec{\mathbf{F}} = \mathbf{0}, \quad (10)$$

$$\nabla \cdot \vec{\mathbf{F}} = \mathbf{G} - \vec{\mathbf{F}} \cdot \vec{\mathbf{F}}, \quad (11)$$

$$(2\vec{\mathbf{F}} \cdot \nabla + \mathbf{G})^\dagger = 2\vec{\mathbf{F}} \cdot \nabla + \mathbf{G}, \quad (12)$$

$$\frac{\partial}{\partial x_\mu} \mathbf{F}_\nu - \frac{\partial}{\partial x_\nu} \mathbf{F}_\mu + [\mathbf{F}_\mu, \mathbf{F}_\nu] = 0. \quad (13)$$

In obtaining (12), we have also made use of the antihermitian character of ∇ .

In atomic units, the nonrelativistic molecular Hamiltonian without spin contains only one parameter, namely the small quantity $1/M$. A quantity such as a matrix element of \mathbf{F}_μ or \mathbf{G} may be zero if required to be so by symmetry, it may be small if it contains a positive power of $1/M$, or it may be large near a singularity. Although one cannot exclude rare cases where the magnitude of a matrix element or its denominator is accidentally small, considerable progress can be made by examining normal molecular situations where such accidents do not occur.

There are at least two ways of getting insight into typical magnitudes of the quantities $\vec{F}_{kj}(R)$. First, from the definition it is clear that

$$\nabla \varphi_j(r, R) = \sum_{k=1}^{\infty} \vec{F}_{kj}(R) \varphi_k(r, R) \quad (14)$$

so that the magnitudes of the \vec{F}_{kj} are intimately related to the magnitude of the gradients of the φ_j . On the other hand, further insight can be gained by an explicit expression for $\vec{F}_{kj}(R)$, gained by differentiating (4) and applying the definition (7)

$$\vec{F}_{kj}(R) = \frac{\langle k(R) | \nabla \hat{H}_{\text{el}}(R) | j(R) \rangle}{V_j(R) - V_k(R)} \quad (k \neq j). \quad (15a)$$

The electronic Hamiltonian, in the atomic units used here, does not contain any large or small parameter such as M or $(1/M)$; all terms in it are of order unity, inherently neither very large nor very small. Accordingly, changes in a coordinate

x_μ that are very small in atomic units will produce no significant change in \hat{H}_{el} ; changes of order unity will produce substantial changes; while changes large compared with unity will produce large changes. Thus, one expects φ_j to change substantially, i.e., by amounts of order unity, when the coordinates change by one Bohr, meaning that $|\nabla \varphi_j|$ in normal molecular situations is expected to be of order unity; and according to (14) this means that at least some of the $\vec{F}_{kj}(R)$ must be of order unity. Looking at (15a), one expects the numerator to be of order unity, and well-behaved as a function of R , while the denominator, an energy difference between electronic levels, will also be of order unity, leading to the same conclusion about the typical magnitude of $\vec{F}_{kj}(R)$. However, (15a) provides us with one situation in which \vec{F}_{jk} can become *large*, namely in the near neighborhood of a degeneracy, when the denominator becomes vanishingly small. On the other hand, one occasionally encounters the statement in the literature that \vec{F}_{jk} will be small if the energy denominators are large enough. Eq. (15a) shows that this is true, but many such denominators will be no larger than order unity in atomic units. A large energy denominator here means a denominator of many Hartree units, something that appears only when one of the states is very highly excited. We see, therefore, that the \vec{F}_{kj} are typically of order unity in normal molecular situations.

Further insight into the coupling can be achieved by considering a component (for example that corresponding to the x coordinate of nucleus A) of Eq. (15a) as

$$(F_{Ax})_{kj}(R) = \frac{\int dr \varphi_k(r, R) (\partial U(r, R) / \partial x_A) \varphi_j(r, R)}{V_j(R) - V_k(R)}, \quad (15b)$$

where $U(r, R)$ denotes the sum of the electronic and nuclear Coulomb interactions. The partial derivative in (15b) is singular only when the coordinates of two particles coincide, but the electron–electron and electron–nucleus singularities are washed out by the integration over r . The singularity when two nuclei coincide depends only on R , and is thus diagonal in the electronic states; and such diagonal elements are not governed by

(15b). Consideration of $\partial U/\partial x_A$ thus adds further weight to our conclusion that $\vec{F}_{kj}(R)$ is never singular or large in atomic units except at or near (respectively) intersections of $V_k(R)$ and $V_j(R)$.

In the traditional BO approach, one isolates one state from the coupled Eq. (6), ignoring the coupling of that state to all the others. Clearly, this would be permissible, e.g., for state 1, if for some region of interest S we had

$$\vec{F}_{k1}(R) = 0 \quad (R \in S, k > 1). \quad (16)$$

(If (16) holds, it is a consequence of (11) that a similar result holds for \mathbf{G} .) If (16) holds, however, it is an immediate consequence of (14) that φ_j does not vary with R at all, remaining “frozen” [13]. This will not happen, even approximately, in normal molecular situations.

Many applications are concerned not with isolating just one electronic state, but two, three, or some other small number, q , of such states. We can call this the generalized BO approximation. For example, these might be the q states of lowest energy. If the q states of interest were uncoupled to the rest of the states, we would have

$$\vec{F}_{jk}(R) = 0, \quad \text{when } j \leq q, k > q. \quad (17)$$

Assuming that (17) holds, consider the projection operator on the space spanned by the q states

$$\hat{P}_q(R) = \sum_{k=1}^q |k(R)\rangle\langle k(R)|. \quad (18)$$

Now consider the variation of the projection operator with R . We find

$$\begin{aligned} \nabla \hat{P}_q(R) &= \sum_{k=1}^q \{ |\nabla k(R)\rangle\langle k(R)| + |k(R)\rangle\langle \nabla k(R)| \} \\ &= \sum_{j=1}^{\infty} \left\{ \sum_{k=1}^q \left[|j(R)\rangle \vec{F}_{jk}(R) \langle k(R)| \right. \right. \\ &\quad \left. \left. + |k(R)\rangle \vec{F}_{jk}^*(R) \langle j(R)| \right] \right\}. \quad (19) \end{aligned}$$

Now, it is easy to see with the aid of (9) that the terms in the sum (19) with $j \leq q$ cancel out; for example, the term in the first sum with $j = 1, k = 2$ is canceled by the one in the second sum with $k = 1, j = 2$. This leaves only the terms with $j > q, k \leq q$. But if (17) holds, these vanish. Thus, if (17)

holds, the projection operator does not vary with R in the region S , remaining frozen

$$\hat{P}_q(R) = \hat{P}_q(R_0) \quad (R, R_0 \in S). \quad (20)$$

Now, since evidently (for $j \leq q$)

$$|j(R)\rangle = \hat{P}_q(R)|j(R)\rangle, \quad (21)$$

we have for $j \leq q$, using (18), (20), and (21):

$$|j(R)\rangle = \hat{P}_q(R_0)|j(R)\rangle = \sum_{k=1}^q |k(R_0)\rangle\langle k(R_0)|j(R)\rangle. \quad (22)$$

Thus, if (17) holds it follows that the electronic eigenstates over the whole region are expressible in terms of a small number q of frozen states. This does not happen, even approximately, in normal molecular situations.

The discussion of Eqs. (16)–(21) shows that assumptions about vanishing (or small) coupling between subspaces in (6) lead to impossible consequences about electronic states remaining frozen (or nearly so). This reinforces the discussion of Eqs. (15a) and (15b), which indicated that one should not look for the justification of the BO or generalized BO approximation in the properties of the \mathbf{F}_μ , which are independent of $1/M$, but rather in the smallness of the $1/M$ prefactors in the third and fourth terms of Eq. (6). To see this more precisely, let us make the definition

$$\hat{\mathbf{Z}} = -\left(\vec{\mathbf{F}} \cdot \nabla + \frac{1}{2} \mathbf{G} \right), \quad (23)$$

and write the Hamiltonian operator on the left of (6) in symbolic matrix form as

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \frac{1}{M} \hat{\mathbf{Z}}. \quad (24)$$

We note that $\hat{\mathbf{H}}_0$ is diagonal in the electronic states, while $\hat{\mathbf{Z}}$ can have both diagonal and off-diagonal elements. We now separate the column vector Ψ of the ψ_k into a portion Ψ_q containing the components $1 - q$ and another portion Ψ_s containing all the others. Similarly, we write the Hamiltonian as

$$\hat{\mathbf{H}} = \begin{pmatrix} \hat{\mathbf{H}}_q & \frac{1}{M} \hat{\mathbf{Z}}_{qs} \\ \frac{1}{M} \hat{\mathbf{Z}}_{sq} & \hat{\mathbf{H}}_s \end{pmatrix}. \quad (25)$$

The eigenvalue Eq. (6) can now be written:

$$\begin{aligned}\hat{\mathbf{H}}_q \Psi_q + \frac{1}{M} \hat{\mathbf{Z}}_{qs} \Psi_s &= E \Psi_q, \\ \frac{1}{M} \hat{\mathbf{Z}}_{sq} \Psi_q + \hat{\mathbf{H}}_s \Psi_s &= E \Psi_s.\end{aligned}\quad (26)$$

The second equation of (26) has the formal solution

$$\Psi_s = (E - \hat{\mathbf{H}}_s)^{-1} \left(\frac{1}{M} \right) \hat{\mathbf{Z}}_{sq} \Psi_q. \quad (27)$$

Thus, we will have $|\Psi_s| \ll |\Psi_q|$ if all of the following are true:

- (i) M is large (it is),
- (ii) the eigenvalues of $\hat{\mathbf{H}}_s$ differ from E by amounts of order unity or more in atomic units (this is true for example if the q states of interest are low-lying electronic states, with the others separated from them by at least a sizable fraction of an atomic unit, and if E is the energy of a low-lying electronic state, plus relatively small rovibrational contributions),
- (iii) any powers of M contained in matrix elements of $\hat{\mathbf{Z}}_{sq}$ are less than 1 (in fact [4,5,14], the highest power contained in such matrix elements is 1/4).

Let us assume that we have a problem in which it is permissible (to a good approximation) to truncate the expansion (3) after q terms. In this case, we can write the eigenvalue Eq. (6) in matrix form, isolating just the part referring to the q states of interest

$$\left\{ -\frac{1}{2M} \left[(\nabla + \vec{\mathbf{F}}^{(q)})^2 + (\vec{\mathbf{F}}^{(\text{od})} \cdot \vec{\mathbf{F}}^{(\text{od})})^{(q)} \right] + \mathbf{V}^{(q)} \right\} \Psi^{(q)} = E \Psi^{(q)}, \quad (28)$$

where $\vec{\mathbf{F}}^{(\text{od})}$ is the part of $\vec{\mathbf{F}}$ that couples the q states of interest to the rest of the space (but which contributes to the q part of $\vec{\mathbf{F}} \cdot \vec{\mathbf{F}}$), and we have made use of (11). The term $(\vec{\mathbf{F}}^{(\text{od})} \cdot \vec{\mathbf{F}}^{(\text{od})})^{(q)}$ would vanish if (17) were satisfied. $\mathbf{V}^{(q)}$ is the diagonal matrix whose elements are the electronic eigenvalues V_j . When one tries to solve (28), one often finds that the terms in $\vec{\mathbf{F}}^{(q)} \cdot \nabla$ are troublesome (because, among other reasons, they can be singular), so that it would be useful to find a transformation that eliminates these terms. Therefore, in the next section, we consider transforming to a nonadiabatic representation.

3. Coupling in nonadiabatic representations

If we write

$$\Psi^{(q)}(R) = \mathbf{S}^{(q)}(R) X^{(q)}(R), \quad (29)$$

where $\mathbf{S}^{(q)}(R)$ is a unitary q -dimensional matrix to be determined, we find that the transformed Eq. (28) contains no terms in ∇X if $\mathbf{S}^{(q)}$ satisfies

$$\nabla \mathbf{S}^{(q)}(R) + \vec{\mathbf{F}}^{(q)}(R) \mathbf{S}^{(q)}(R) = 0. \quad (30)$$

If one can solve Eq. (30), the resulting representation in terms of the components of $X^{(q)}$ is called a strictly diabatic representation (SDR). (It is important to make the distinction between a ‘‘strictly diabatic’’ representation obtained from an exact solution of (30), and an ‘‘approximately diabatic’’ or ‘‘quasi-diabatic’’ one, resulting from an approximate solution, although the latter are often just called ‘‘diabatic’’ to avoid being pedantic.) It is well known that quasi-diabatic representations are very useful for a wide variety of applications [15–20], but our concern here is with the question of the existence of SDRs, a question that is also widely discussed, but sometimes misinterpreted.

Eq. (30) takes a particularly simple form in the common case in which $q = 2$ and the states involved can be taken to be real. In this case we have

$$\vec{\mathbf{F}}^{(2)}(R) = \begin{pmatrix} 0 & \vec{f}(R) \\ -\vec{f}(R) & 0 \end{pmatrix}. \quad (31)$$

The most general form of $\mathbf{S}^{(q)}(R)$ is

$$\mathbf{S}^{(q)}(R) = \begin{pmatrix} \cos \lambda(R) & \sin \lambda(R) \\ -\sin \lambda(R) & \cos \lambda(R) \end{pmatrix}, \quad (32)$$

and (30) reduces to

$$\nabla \lambda(R) + \vec{f}(R) = 0. \quad (33)$$

Suppose there is a second solution of (30)

$$\bar{\mathbf{S}}^{(q)}(R) = \mathbf{S}^{(q)}(R) \mathbf{U}^{(q)}(R), \quad (34)$$

where $\mathbf{U}^{(q)}(R)$ is again a unitary matrix. (Since $\mathbf{S}^{(q)}$ and $\bar{\mathbf{S}}^{(q)}$ are both unitary, they must satisfy a relation such as (34).) Requiring that $\bar{\mathbf{S}}^{(q)}$ also satisfy (30) leads to the requirement

$$\nabla \mathbf{U}^{(q)}(R) = 0. \quad (35)$$

In other words, \mathbf{U} must be a constant matrix. If $q = 2$, this reduces to the familiar result that two solutions of (33) can differ at most by an additive constant.

One obtains a necessary and sufficient condition for the existence of a solution of (30) by equating second partial derivatives

$$\frac{\partial}{\partial x_\mu} \mathbf{F}_\nu^{(q)} - \frac{\partial}{\partial x_\nu} \mathbf{F}_\mu^{(q)} + [\mathbf{F}_\mu^{(q)}, \mathbf{F}_\nu^{(q)}] = 0, \quad (36)$$

where x_μ and x_ν are shorthand for nuclear coordinates like x_A and y_B . If (36) is satisfied, then there is an SDR, otherwise not. Eq. (36) resembles (13), but it is different because of the contribution of the off-diagonal terms introduced in (28), and this difference is critical. Indeed it is easy to see from (13) that

$$\frac{\partial}{\partial x_\mu} \mathbf{F}_\nu^{(q)} - \frac{\partial}{\partial x_\nu} \mathbf{F}_\mu^{(q)} + [\mathbf{F}_\mu^{(q)}, \mathbf{F}_\nu^{(q)}] = -[\mathbf{F}_\mu^{(\text{od})}, \mathbf{F}_\nu^{(\text{od})}]^{(q)}. \quad (37)$$

Thus, we have a strictly diabatic basis if and only if the right-hand side of (37) vanishes; in this case, as we have seen above, the solution of (30) is unique up to a constant matrix. If (36) is not satisfied, then (30) has no solutions, unique or otherwise. If $q = 2$, and (30) is replaced by (33), then the requirement (36) reduces to the well-known result that the curl of a gradient must be zero [21].

As we have seen in the previous section, the matrix elements making up the right side of (37) are not zero or small in normal molecular situations, and the same will normally be true of the commutator. A priori, as with the case of the matrix elements themselves, there is no reason to expect the right side of (37) to be either very large or very small; any claim that it is so in a particular case must be justified for that case.

Thus SDRs do not exist [21,22], although there may exist nonunique quasi-diabatic representations which are useful in certain problems. In the two-state case, one can always express \vec{f} as a sum of a removable irrotational part with zero curl, and a nonremovable solenoidal part [21]. Moreover, there are cases in which the removable part is the larger and/or the more troublesome of the two. In particular, the part that becomes singular as one

approaches a conical intersection, which is frequently the most important part, is always removable [21], as we now proceed to show.

The above analysis allows us to provide a general criterion for when the singularity in the coupling is removable. From the discussion of Eqs. (15a) and (15b), it is clear that the q states selected for applying the generalized BO approximation should not exclude any states whose energies intersect or come close to those of an included one. When this criterion for state selection is heeded, $|V_k(R) - V_j(R)|$ is of the order of magnitude of unity or greater in atomic units when $k > q$ and $j \leq q$. Then we consider the right-hand side of Eq. (37), which is the part that determines the nonremovability of the nonadiabatic coupling. This expression consists entirely of elements of the $\bar{\mathbf{F}}$ matrices that connect included states with excluded ones. We have thus concluded that when the states used in the generalized BO approximation are selected properly, the energy gaps between such pairs of states are all appreciable; hence we conclude that the nonremovable elements of $\bar{\mathbf{F}}$ cannot be singular or even very large. Thus any singular part of the coupling satisfies (30), and is thus removable.

In summary, our analysis has shown that the singular coupling is removable, but in normal molecular situations, apart from the singularity, the removable and nonremovable parts of the coupling can be expected to be of the same order of magnitude.

The above analysis can also be used to shed light on some treatments already in the literature. For example, one treatment [12] uses Eq. (17) as the justification for truncating the series in (3), but we have shown that the correct justification is the smallness of $1/M$ combined with the criterion that any states whose energies intersect or come close to included ones should not be excluded. Furthermore, if (17) were satisfied, then the relations Eqs. (9)–(13) would be satisfied even for the truncated submatrices restricted to the selected q states, $\mathbf{F}_\mu^{(q)}$, $\mathbf{G}^{(q)}$, etc. Actually, relations (10), (11), and (13) do not hold for the submatrices, since for example $(\bar{\mathbf{F}} \cdot \bar{\mathbf{F}})^{(q)} \neq \bar{\mathbf{F}}^{(q)} \cdot \bar{\mathbf{F}}^{(q)}$. This error causes Eq. (16) of [12] to be incorrect, and the same problem crops up elsewhere as well. The miscon-

ception of attributing the validity of the BO procedure to the smallness of the off-diagonal $\bar{\mathbf{F}}$ matrix elements, rather than to the smallness of $(1/M)$, is a problem that regrettably occurs in other contexts as well. For example [23], this misconception has led to the imposition of “auxiliary conditions” on the nuclear wave functions, which need not be imposed if a consistent $(1/M)$ analysis is performed. Fortunately, the main conclusions of [23] are not affected by this misconception.

Eq. (30) is also relevant to previous work, where it is stated that this equation is a condition for the uniqueness of \mathbf{S} and it is implied or assumed that it can be satisfied or perhaps that it can be satisfied except at isolated singularities [12,24–26]. With this assumption it is shown that SDRs are obtained only if the physical problem satisfies certain quantization conditions [12,25]. However, Eq. (30) is actually a condition for the existence of \mathbf{S} , and it is not satisfied even in regions that do not contain singularities [21,27]. The arguments presented here have shown that the restricted set of electronic Hamiltonians allowing SDRs does not include normal molecular situations. Integration of the irrotational part of the nonadiabatic coupling around a closed path will give a multiple of π . This result was implicit in some of the earlier work [28,29], and has been explicitly demonstrated by Yarkony [30]. If the path is allowed to become vanishingly small, the contribution of the solenoidal part becomes negligible, so the integration of the entire nonadiabatic coupling will approach a multiple of π , usually just π or zero, depending on whether the path does or does not surround a conical intersection. Integration of the entire nonadiabatic coupling around finite-sized paths in normal molecular situations will show nonnegligible deviations from the “quantization” result as the nonremovable solenoidal part becomes important. Numerical calculations confirm this expectation [30–34]. In the foregoing discussion, we have used language appropriate to the case of $q = 2$, with three nuclear coordinates of interest. The conclusions, however, remain valid for other cases as well.

One can construct models [35,36] in which SDRs exist by construction. This illustrates how terms that are essentially never zero may some-

times be negligible for particular purposes. Arguments about whether nonzero terms are negligible for specific problems may be made on a case-by-case basis, and quasi-diabatic representations may be useful, as stated above.

4. Approximations to the coupled equations

Consider the two-state case. With $\bar{\mathbf{F}}$ given by (31) and neglecting $\bar{\mathbf{F}}^{(\text{od})} \cdot \bar{\mathbf{F}}^{(\text{od})}$, which is irrelevant in this section, Eq. (28) takes the form

$$\begin{aligned} & \left(-\frac{1}{2M} \nabla^2 + \bar{V}_1 - E \right) \psi_1 \\ & - \frac{1}{2M} [2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})] \psi_2 = 0, \\ & \left(-\frac{1}{2M} \nabla^2 + \bar{V}_2 - E \right) \psi_2 \\ & + \frac{1}{2M} [2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})] \psi_1 = 0, \end{aligned} \quad (38)$$

where

$$\bar{V}_j = V_j - \frac{1}{2M} f^2, \quad j = 1, 2. \quad (39)$$

Since the differential equations (38) have real coefficients, one can, without loss of generality, restrict oneself to real solutions of (38). Any solution is either a constant multiple of a real solution (if nondegenerate) or a linear combination of real solutions with constant coefficients (if degenerate). The constant coefficients may of course take on complex values, but this does not affect the conclusion. An analysis similar to that of Section 2, Eqs. (23)–(27), adapted to a two-state Hilbert space, shows that ψ_2 will be small if V_1 and V_2 are well separated and if E differs from V_1 only by relatively small contributions of the nuclear motion. A consistent approximation based on the smallness of ψ_2 would be to neglect all terms involving ψ_2 (or all in which ψ_2 or its derivatives appear multiplied by $1/M$). The neglect of all terms in ψ_2 gives us the familiar one-state BO approximation, which is indeed a good approximation (to lowest order in $1/M$) when the criterion derived above for its validity is satisfied.

It is instructive to compare this to an alternative approach. In that approach [12,37] one makes the transformation

$$\begin{aligned}\psi_1 &= \frac{1}{\sqrt{2}}(\chi_1 + \chi_2), & \psi_2 &= \frac{i}{\sqrt{2}}(\chi_1 - \chi_2), \\ \chi_1 &= \frac{1}{\sqrt{2}}(\psi_1 + i\psi_2), & \chi_2 &= \frac{i}{\sqrt{2}}(\psi_1 - i\psi_2),\end{aligned}\quad (40)$$

which yields the result

$$\begin{aligned}\left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E + \frac{i}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\right)\chi_1 \\ + \left\{\frac{1}{2}(\bar{V}_2 - \bar{V}_1)(\chi_1 - \chi_2)\right\} = 0, \\ \left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E - \frac{i}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\right)\chi_2 \\ - \left\{\frac{1}{2}(\bar{V}_2 - \bar{V}_1)(\chi_1 - \chi_2)\right\} = 0.\end{aligned}\quad (41)$$

Inspection of (41) shows that one can restrict oneself without loss of generality to solutions in which $\chi_2 = \chi_1^*$. Such solutions are equivalent to the real solutions of (38). It has been argued [12] that, if \bar{V}_2 lies well above \bar{V}_1 , and if E is substantially less than \bar{V}_2 , then $\psi_2 = (i/\sqrt{2})(\chi_1 - \chi_2)$ will be small, justifying the neglect of the terms in curly brackets in (41), an approximation that has been widely employed [12,37]. If this is permitted, it leads to the uncoupled equations [12]

$$\begin{aligned}\left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E + \frac{i}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\right)\chi_1 \\ = 0, \\ \left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E - \frac{i}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\right)\chi_2 \\ = 0.\end{aligned}\quad (42)$$

In terms of the original components ψ_1 and ψ_2 , Eq. (41) becomes

$$\begin{aligned}\left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E\right)\psi_1 - \frac{1}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\psi_2 \\ = 0, \\ \left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E\right)\psi_2 + \frac{1}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\psi_1 \\ + \{(\bar{V}_2 - \bar{V}_1)\psi_2\} = 0.\end{aligned}\quad (43)$$

When the term in curly brackets is omitted, as in (42), one has

$$\begin{aligned}\left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E\right)\psi_1 - \frac{1}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\psi_2 \\ = 0, \\ \left(-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E\right)\psi_2 + \frac{1}{2M}[2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})]\psi_1 \\ = 0.\end{aligned}\quad (44)$$

This approximation involves neglecting those terms in which ψ_2 is multiplied by $(\bar{V}_2 - \bar{V}_1)$, while keeping the smaller terms in which it or its derivatives are multiplied by $1/M$ or by $(\bar{V}_1 - E)$, which is also small under the stated conditions [12,37]. Moreover, these kept terms play a crucial role in the subsequent analysis. Neglecting $(\bar{V}_2 - \bar{V}_1)\psi_2$ is not based on a consistent analysis of the consequences of the smallness of ψ_2 . In fact the largeness of $(\bar{V}_2 - \bar{V}_1)$ compared with energies of nuclear motion is required to justify the assumed smallness of ψ_2 . The present analysis is consistent with one presented previously [14], where it was shown that the neglected term is larger than some of the important retained terms. It was also shown [14] (making use of the real nature of the solutions of (38)) that in the cases of most interest the solutions of (44) contradict the original assumption of small ψ_2 .

It has been proposed [12] that requiring $\chi_2 = \chi_1$ will lead to solutions of Eq. (43) that are in accord with the assumed smallness of ψ_2 . This would mean that χ_1 satisfies both equations of (42). It is claimed in [12] that this can be achieved. However, if χ_1 satisfies both equations of (43), then addition and subtraction of the two equations gives

$$\begin{aligned}\left\{-\frac{1}{2M}\nabla^2 + \bar{V}_1 - E\right\}\chi_1 = 0, \\ \{2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})\}\chi_1 = 0,\end{aligned}\quad (45)$$

i.e., χ_1 would have to be simultaneously an eigenfunction of the two noncommuting operators $\{-(1/2M)\nabla^2 + \bar{V}_1 - E\}$ and $\{2\vec{f} \cdot \nabla + (\nabla \cdot \vec{f})\}$. We conclude that the inconsistency of Eq. (41) cannot be circumvented in this way.

It has been proposed [38] that one can improve on Eqs. (42) and (44) by setting \bar{V}_2 equal to \bar{V}_1 only near the intersection. Certainly it is true that, in a very small region, some features of the problem

are insensitive to the difference in potential energies; but even here, the most distinctive feature is the conical nature of the intersection, which is missed in this approach. Furthermore, in the near neighborhood of an intersection, one cannot assume small ψ_2 .

5. Geometric phase

It was pointed out by Herzberg and Longuet-Higgins (HL) [9] that an electronic eigenfunction that is required to be real and smooth as a function of R undergoes a sign change when transported continuously around a conical intersection between two electronic potential energy surfaces. This sign change is a special case of the “geometric phase” which sometimes appears when a quantum mechanical eigenfunction is transported around a closed path [6–11]. This means that real electronic wave functions are not single-valued as functions of R , and this in turn will cause the full molecular wave function given by (3) or approximately by (1) to also fail to be single-valued unless something is done [10]. Basically, there have been two equivalent approaches to this problem: (i) One may cancel the HL sign change in $\varphi_j(R, r)$ by changing the boundary conditions on the nuclear wave function $\psi_j(R)$ so that it also changes sign on traversal of a path around a conical intersection; or (ii) one may multiply $\varphi_j(R, r)$ by an R -dependent phase factor which cancels the sign change [10]. The phase angle of this phase factor is sometimes called the HL angle. The rephased φ_j will still satisfy (4) and (5), so this change is permissible, and it involves no approximation if carried out consistently. This rephasing, however, does affect the matrix elements of $\vec{\mathbf{F}}$ and \mathbf{G} ; in particular, there are now nonzero diagonal elements of $\vec{\mathbf{F}}$, which introduce vector potential-like terms into the effective Hamiltonian satisfied by ψ_j . Since the HL phase factor $e^{i\theta(R)}$ only has to cancel the sign change, the only requirement on $\theta(R)$ is that it be real and advance by an odd multiple of π on circum-navigation of a conical intersection. Thus, a completely equivalent formulation is obtained (also without any approximation) if $\theta(R)$ is replaced by

$$\bar{\theta}(R) = \theta(R) + \eta(R), \quad (46)$$

where $\eta(R)$ is any real function such that $e^{i\eta(R)}$ is single-valued. Eq. (46) is sometimes called a gauge transformation, and such a transformation also affects matrix elements of $\vec{\mathbf{F}}$ and \mathbf{G} ; in particular, the effective vector potential undergoes a gauge transformation of the kind familiar in electromagnetic theory [10].

The HL angle always exists, whereas an adiabatic–diabatic transformation angle λ satisfying Eq. (33) does not exist for real molecular situations. There is, however, a set of model problems for which λ exists, and in which θ , with an appropriate choice of gauge, can be set equal to λ . It is also possible to construct models in which λ exists, but where it is impossible to have $\theta = \lambda$ [14]. In general, there is much flexibility in θ , which can also be altered by an arbitrary gauge transformation (46), whereas λ must satisfy Eq. (33), which only permits the addition of a constant (λ is not subject to gauge transformations). Some of these considerations are sometimes stated incorrectly [12].

The rephasing approach based on the geometric phase [10] is designed to handle the sign change of the electronic wave function on traversal of a closed path around the intersection, but it does not handle the state coupling. There has been some discussion in the literature [28,29,39] of the case in which both the sign change and the coupling must be considered.

Aharonov et al. [40] solved a simple model of the BO problem in which the electronic degrees of freedom are replaced by a single spin, acted on by a magnetic field which is constant in magnitude but whose direction follows the coordinates of a heavy particle. This leads to a somewhat different way of looking at the BO approach and gives useful insight. This paper is sometimes cited to support incorrect conclusions related to the concerns of the present paper, and therefore it merits discussion here. We note first that [40] has the “electronic” Hilbert space restricted to $(2s + 1)$ dimensions, so that any state can be expressed as a linear combination of $(2s + 1)$ frozen states, and furthermore the separation of the electronic energy levels is strictly maintained. Because the “elec-

tronic” Hilbert space is finite, a strictly diabatic basis exists by construction in this model, though not in normal molecular situations. With the magnetic field present, the traversal of a closed path with a requirement of zero diagonal F_μ along the path can lead to an arbitrary phase change in the “electronic” wave function, rather than just a sign change or no change as in the cases discussed here. There is no single ADT angle, but rather an ADT transformation involving two angles. The vector potential would arise in this model, as elsewhere in the literature [8], as a result of requiring that the “electronic” wave function be single-valued. In [40] attention is called to the fact that the geometric phase in a single “electronic” (spin in the model of [40]) state is caused by the terms coupling it to other states. In our formulation, this says that there would be no geometric phase or HL sign change if Eq. (16) were satisfied. The results of [40] all appear to be correct for the model specified, and they are not claimed to apply to normal molecular situations, which have different properties.

6. Concluding remarks

We have shown that for normal molecular situations one cannot expect the nonadiabatic coupling terms in the BO representation to be either very large or very small compared to unity in atomic units. The chief exception occurs at and near conical intersections where the nonadiabatic coupling is singular. We have also analyzed the effect of an orthogonal transformation of the BO basis states on the couplings between the electronic states, and we showed that the residual coupling in general has the same order of magnitude as the nonadiabatic coupling in the BO representation, except that the singularities at conical intersections and the large values near conical intersections are no longer required (provided that the energies of the chosen electronic states in the BO representation remain well separated from those of the excluded states).

Thus one can find new electronic representations that reduce the coupling everywhere to a level comparable to the nonadiabatic coupling that

occurs in the BO representation in regions where the BO approximation is a good approximation. Furthermore the analysis shows that one cannot do systematically better than this, i.e., there is no privileged representation in which aside from considerations specific to a particular molecular system, the coupling is systematically smaller than the normal BO breakdown terms. This is not an impediment to studying low-energy molecular eigenvalues since the BO approximation is very good in normal molecular situations. Furthermore, it means that all nonadiabatic (i.e., diabatic, quasi-diabatic) representations are equally formally justified, provided that they remove the singularities in the adiabatic representation, and one may choose between them on the basis of convenience for a specific application or aptness for a particular molecular situation.

Acknowledgements

We are grateful to Horst Köppel and D.R. Yarkony for helpful comments; to A. Kuppermann and D.R. Yarkony for allowing us access to the results of [33] prior to publication; and additionally to A. Kuppermann for similarly allowing us access to [34]. This work was supported in part by the National Science Foundation under grant no. CHE00-92019. Part of this work was done under the auspices of the US Department of Energy under Project No. 990015 of the Laboratory Directed Research and Development program at Los Alamos under Contract No. W-7405-ENG-36.

References

- [1] M. Born, K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University Press, New York, 1954.
- [2] C.J. Ballhausen, A.E. Hansen, *Annu. Rev. Phys. Chem.* 23 (1972) 15.
- [3] H. Köppel, W. Domcke, L.S. Cederbaum, *Adv. Chem. Phys.* 57 (1984) 591.
- [4] C.A. Mead, in: D.G. Truhlar (Ed.), *Mathematical Frontiers in Computational Chemical Physics*, Springer, New York, 1988, p. 1.
- [5] M. Born, R. Oppenheimer, *Ann. Phys.* 84 (1927) 457.
- [6] A. Shapere, F. Wilczek (Eds.), *Geometric Phases in Physics*, World Scientific, Singapore, 1989.

- [7] J.W. Zwanziger, M. Koenig, A. Pines, *Annu. Rev. Phys. Chem.* 41 (1990) 601.
- [8] C.A. Mead, *Rev. Mod. Phys.* 64 (1992) 51.
- [9] G. Herzberg, H.C. Longuet-Higgins, *Discuss. Faraday Soc.* 35 (1963) 77.
- [10] C.A. Mead, D.G. Truhlar, *J. Chem. Phys.* 70 (1979) 2284.
- [11] M.V. Berry, *Proc. R. Soc. London, Ser. A* 392 (1984) 45.
- [12] M. Baer, *Chem. Phys.* 259 (2000) 123.
- [13] B. Andresen, S.E. Nielsen, *Mol. Phys.* 21 (1971) 523.
- [14] B.K. Kendrick, C.A. Mead, D.G. Truhlar, *J. Chem. Phys.* 110 (1999) 7594.
- [15] W. Lichten, *Phys. Rev.* 131 (1963) 229.
- [16] T.F. O'Malley, *Adv. At. Mol. Phys.* 7 (1971) 223.
- [17] B.C. Garrett, D.G. Truhlar, *Theor. Chem. Adv. Perspect.* 6A (1981) 216.
- [18] J.B. Delos, *Rev. Mod. Phys.* 53 (1981) 287.
- [19] V. Sidis, *Adv. Chem. Phys.* 82 (1992) 73.
- [20] T. Pacher, L.S. Cederbaum, H. Köppel, *Adv. Chem. Phys.* 84 (1993) 293.
- [21] C.A. Mead, D.G. Truhlar, *J. Chem. Phys.* 77 (1982) 6090.
- [22] A.D. McLachlan, *Mol. Phys.* 4 (1961) 417.
- [23] A. Bohm, B. Kendrick, M.E. Loewe, L.J. Boya, *J. Math. Phys.* 33 (1992) 977.
- [24] M. Baer, A.J.C. Varandas, R. Englman, *J. Chem. Phys.* 111 (1999) 9493; *J. Chem. Phys.* 112 (2000) 6089.
- [25] M. Baer, A. Aljiah, *Chem. Phys. Lett.* 319 (2000) 489.
- [26] M. Baer, *Chem. Phys. Lett.* 347 (2001) 149.
- [27] B.K. Kendrick, C.A. Mead, D.G. Truhlar, *Chem. Phys. Lett.* 330 (2000) 629.
- [28] C.A. Mead, *J. Chem. Phys.* 78 (1983) 807.
- [29] T.C. Thompson, C.A. Mead, *J. Chem. Phys.* 82 (1985) 2408.
- [30] D.R. Yarkony, *J. Chem. Phys.* 105 (1996) 10456.
- [31] N. Matsunaga, D.R. Yarkony, *J. Chem. Phys.* 107 (1997) 7825.
- [32] R.D. Sadygov, D.R. Yarkony, *J. Chem. Phys.* 109 (1998) 20.
- [33] R. Abrol, A. Shaw, A. Kuppermann, D.R. Yarkony, *J. Chem. Phys.* 115 (2001) 4640.
- [34] R. Abrol, A. Kuppermann, *J. Chem. Phys.* 116 (2002) 1035.
- [35] P. Halvick, D.G. Truhlar, *J. Chem. Phys.* 96 (1992) 2895; Erratum: *J. Chem. Phys.* 100 (1994) 4718.
- [36] M.D. Hack, D.G. Truhlar, *J. Chem. Phys.* 110 (1999) 4315.
- [37] M. Baer, R. Englman, *Chem. Phys. Lett.* 265 (1997) 105; M. Baer, *J. Chem. Phys.* 107 (1997) 2694.
- [38] A.J.C. Varandas, Z.R. Xu, *J. Chem. Phys.* 112 (2000) 2121.
- [39] T.C. Thompson, D.G. Truhlar, C.A. Mead, *J. Chem. Phys.* 82 (1985) 2392.
- [40] Y. Aharonov, E. Ben-Reuven, S. Popescu, D. Rohrlich, *Nucl. Phys. B* 350 (1991) 818.