Quasi-diabatic basis versus fixed electronic states in molecular systems

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Abstract: We consider the use of quasi-diabatic bases to improve upon the Born-Oppenheimer approximation in molecular systems. In a nonrigorous, but still suggestive, manner, it is shown that, when the quasi-diabatic approximation is a good one, the use of “frozen” electronic states will often be equally good, or nearly so.

1. Introduction

A problem that has received much attention in molecular theory is the best way to handle the so-called nonadiabatic coupling terms (NACTs) between different Born-Oppenheimer electronic states. An approach that has been often used is to construct, as nearly as possible, a so-called diabatic basis, a basis of electronic states which are linear combinations of a finite number of Born-Oppenheimer states, chosen in such a way that the NACTs vanish with respect to the new states. The transformation that achieves this is called the adiabatic to diabatic transformation, or ADT. The approach has been nicely described, with further references, by Baer [1].

However, it has also been shown [2,3] that an exact ADT does not, in general, exist, so that one must content oneself with trying to construct useful approximations. In this note, we present a nonrigorous analysis of when this is feasible, and in such cases, how the ADT compares with the simple use of frozen electronic states (FS), independent of the nuclear coordinates.

In Section 2, we introduce the notation and present the “curl condition” for the existence of an exact ADT. In Section 3, we show that this condition is the same as that for the exact use of FS. Section 4 contains a rough analysis of the two approaches when neither is exactly true. There is a brief discussion in Section 5. Much of our analysis is similar to what has been presented elsewhere [2,3] but from a somewhat different point of view. Throughout, we use atomic units.

2. Diabatic basis

We consider the subspace $S$ of the electronic Hilbert space $H$, spanned by $n$ Born-Oppenheimer electronic states $|\alpha(R)\rangle$, where $R$ is the space of the nuclear coordinates. The NACT matrix $\tau_j(R)$ is defined by

$$\langle \alpha | \tau_j | \beta \rangle = \langle \alpha | \partial_j | \beta \rangle$$

(1)

where $j$ is any one of the nuclear coordinates.

A diabatic basis is a basis of kets $|\bar{\alpha}\rangle$ defined by
\[ |\alpha\rangle = \sum_j |\gamma_i\rangle \gamma^{\dagger}_{\alpha_j} \]  \hspace{1cm} (2)

such that

\[ \langle \alpha | \bar{\tau}_j | \beta \rangle \equiv \langle \bar{\alpha} | \bar{\partial}_j \bar{\beta} \rangle = 0 . \]  \hspace{1cm} (3)

It can easily be shown [1] that the matrix \( A \) must satisfy

\[ \partial_j A = -\tau_j A . \]  \hspace{1cm} (4)

Furthermore, if \( A \) is to satisfy (4) and be “locally single-valued”, i.e. single-valued upon being taken around an infinitesimal closed curve not surrounding a singularity, we must have the “curl condition”

\[ \partial_k \tau_j - \partial_j \tau_k + \tau_k \tau_j - \tau_j \tau_k = 0 . \]  \hspace{1cm} (5)

Equation (5) is the necessary and sufficient condition for the existence of an exact ADT.

3. Consequences of curl condition

In this section, we assume that we have a basis of electronic kets over the entire HS, including SS and its reciprocal space RS, which are required to be locally single-valued. We define a matrix \( T \) over HS as

\[ \langle \alpha | T_j | \beta \rangle = \langle \alpha | \bar{\partial}_j \bar{\beta} \rangle . \]  \hspace{1cm} (6)

The necessary and sufficient condition for local single-valuedness is now

\[ \partial_k T_j - \partial_j T_k + T_k T_j - T_j T_k = 0 . \]  \hspace{1cm} (7)

We can divide the matrix \( T \) into its parts referring to SS (\( \tau \)), RS (\( S \)), and the parts coupling SS and RS (\( t \)) as follows:

\[ T_j = \begin{pmatrix} \tau_j & t_j \\ -t_j^\dagger & S_j \end{pmatrix} . \]  \hspace{1cm} (8)

The part of (7) that refers to SS is

\[ \partial_k \tau_j - \partial_j \tau_k + \tau_k \tau_j - \tau_j \tau_k - t_k t_j^\dagger + t_j t_k^\dagger = 0 . \]  \hspace{1cm} (9)
Equations (7) and (9) are rigorous, depending only on the local single-valuedness of the basis kets. If there is to be an exact ADT, the curl condition (5) must also be satisfied. Subtracting (5) from (9), we obtain

$$t_j t_k^\dagger - t_k t_j^\dagger = 0.$$  

Equation (10) is thus equivalent to the curl condition, and is necessary and sufficient for the existence of an exact ADT in SS.

There are basically two ways for (10) to be satisfied (or approximately satisfied), viz: (i) the elements of the $t$-matrices vanish (or are small); or (ii) the elements are neither zero nor small, but the combination in (10) cancels to zero (or a small number). Although possibility (ii) cannot be rigorously ruled out, it does require such a fortuitous cancellation that its appearance in any actual molecular context must be extremely unlikely. Certainly any claim that we have (ii) in a real case would require proof. Hence, we will dismiss (ii) and concentrate on (i) as the only way in which an ADT in SS can exist.

For a diabatic basis to exist, then, we must have

$$t_j = 0,$$  

i.e.

$$\langle \kappa | \partial_j | \alpha \rangle = 0$$  

for any $|\kappa\rangle$ in RS and $|\alpha\rangle$ in SS. It is also easy to see that the projection operator on SS,

$$P_{SS} = \sum_{\alpha=1}^{n} |\alpha\rangle \langle \alpha|$$  

must be independent of the nuclear coordinates, and thus so must SS itself. If $|\alpha\rangle$ is a ket of a diabatic basis, however, we also have for any $|\beta\rangle$ in SS

$$\langle \beta | \partial_j | \alpha \rangle = 0.$$  

The derivatives of the diabatic kets are thus orthogonal to all vectors in HS, and the diabatic kets are independent of the nuclear coordinates. They are frozen states, FS.

Thus, if a diabatic basis exist at all, it is unnecessary to try to integrate eq. (4) to find it. One just needs to find a basis in SS for some $\mathbf{R}$, and then use those frozen kets for all $\mathbf{R}$. 
4. Approximate validity of ADT or FS
What, however, if the \( t \)-matrix elements are not exactly zero, but are small, say of order \( \varepsilon \)? This would mean in effect that the length scale for significant change in \( P_{SS} \) must be of order \( 1/\varepsilon \). A glance at eq. (9) then shows that the length scale applying to the \( r \)-matrix elements must also be of order \( 1/\varepsilon \). This means that the electronic states of interest are insensitive to changes in nuclear coordinates of order of a few bohr or less, meaning that FS is also a good approximation for regions of dimensions no more that a few bohr. Such a condition is best satisfied for Rydberg states. For such states, the separation of nuclear energy levels is also small, and it is also unclear that the nonremovable part of the NACT will be small compared with the removable part.

Our rough analysis shows that, in many cases if not most when ADT delivers a good approximation, the ADT and FS approaches do not differ significantly from each other in results, as long as one considers a region in nuclear space of dimension no more than a few bohr, i.e. small compared with the length scale \( 1/\varepsilon \), and thus there is no need to make the much greater computational effort required by ADT. For larger regions, or order \( 1/\varepsilon \), the projection operator \( P_{SS} \) will change significantly, and the FS approach will fail.

5. Discussion
Our rough analysis indicates that there are many cases in which the existence of an accurate ADT also requires that the FC approach must be equally accurate in terms of order of magnitude. It must be emphasized, however, that this rough analysis is not rigorous for all cases, and also does not deal with possibility (ii) of Sec. 3. There may thus be real cases in which the ADT approach is most worthwhile.

References

[1] Baer M 2002 Phys. Rep. 358 75
[2] McLachlan A D 1961 Mol. Phys. 4 417
[3] Mead C A and Truhlar D G 1982 J. Chem. Phys. 77 6090