

Diatomics in molecules: A simplified approach

J. A. Olson and B. J. Garrison^{a)}

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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A simplified procedure for obtaining matrix elements in the diatomics in molecules scheme is presented. An essential advantage in this approach is that it avoids partitioning the antisymmetrizer. This allows the components of the valence bond wave functions, i.e., determinants, to be used as fundamental quantities and leads to a transparent method of obtaining matrix elements of the atomic and diatomic Hamiltonians. Two examples, one with five electrons and five nuclei and one with six electrons and five nuclei, are formally treated.

I. INTRODUCTION

As the interest in examining scattering processes for many atom systems (e.g., a particle scattering from a solid surface) has increased, there has been a growing need for a method to easily generate realistic potential surfaces. The application of electronic structure techniques (Hartree-Fock, CI, CNDO, etc.) to these systems is often not feasible due to both the large number of electrons and the numerous geometrical arrangements of nuclei for which the energy must be calculated. One approach for generating potential surfaces is the diatomics in molecules (DIM) scheme.¹ Here information about the diatomic and atomic fragments is used to construct the potential energy surfaces of the polyatomic. Most of the formulations, however, are rather cumbersome and involve the generation of numerous transformation matrices.¹⁻³ For example, in some of the procedures, each diatomic or atomic fragment Hamiltonian is, in general, expressed as a product of nine matrices, four of which result from the partitioning of the antisymmetrizer. For a system of N nuclei, there are $N(N-1)/2$ diatomic Hamiltonians and N atomic Hamiltonians so that a total of $9N(N+1)/2$ matrices need to be constructed. The dimensions of these matrices are related to the number of valence bond basis functions so that implementing these procedures to rather complicated systems can become quite difficult. Our formulation has no partitioning of the antisymmetrizer so that the atomic and diatomic Hamiltonians are expressed as a product of five matrices. This allows the determinants of the atomic spin orbitals to be used directly as the fundamental quantities which leads to a very straightforward way of obtaining matrix elements of the Hamiltonian between valence bond structures. Although Steiner *et al.*⁴ have applied a similar method to the triatomic H_3 system, here we present the general approach for more complicated systems.

The DIM procedure was originally introduced by Ellison¹ and has been further examined by many other researchers.²⁻⁵ Thorough reviews of this subject are given in Refs. 6 and 7. Faist and Muckerman³ have recently compared the various approaches and have addressed the mathematical problems such as non-Hermiticity of the Hamiltonian and overcompleteness of the basis set. We do not address these aspects, but assume from the outset that the basis functions form a linearly independent and complete set. The atomic and diatomic eigenvalue problems are assumed not to intro-

duce any components that are orthogonal to the original polyatomic valence bond basis set. These assumptions result in a well defined linear algebra.

Rather than presenting a general development of the DIM procedure, we instead place our emphasis on how to obtain the matrix representations of the diatomic and atomic Hamiltonians. Special emphasis is placed on minimizing the introduction of new mathematical formalism. At the risk of being a bit ambiguous in places, it should nevertheless aid in providing a clear understanding of how the matrix elements are obtained. A brief development of the formalism is given in Sec. II. The examples of obtaining typical matrix elements given in Sec. III are taken from our ultimate interest in scattering of atoms from metal surfaces. The first system, five electrons and five nuclei, demonstrates the use of covalent bond structures. The second system, six electrons and five nuclei, provides an example of configuration interaction. A discussion of the procedure is given in the final section.

II. GENERAL FORMALISM

In the DIM scheme, the solutions of the electronic Hamiltonian are expressed in terms of a basis set of valence bond wave functions. These basis functions are in turn written as a linear combination of Slater determinants consisting of spin orbitals centered on specific nuclei. If the valence bond basis is linearly independent and complete, so is the set of Slater determinants. The procedure below consists of two stages. The first deals with the general form of a Slater determinant in order to show how they can be reexpressed in a convenient way. The second utilizes the linear independence and completeness of the set in order to obtain a general expression for the effect of a diatomic Hamiltonian on an arbitrary determinant. Since the treatment for the atomic Hamiltonian is the same, it will not be presented here.

The system consists of N nuclei labeled as $1, 2, \dots, N$ and n electrons labeled as $1, 2, \dots, n$. Furthermore, nucleus 1 has n_1 electrons labeled as $1, 2, \dots, n_1$, nucleus 2 has n_2 electrons labeled as $n_1 + 1, n_1 + 2, \dots, n_1 + n_2$ and so on. For convenience of notation let Π_i represent a simple product of atomic spin orbitals centered on nucleus i , i.e.,

$$\Pi_i = i_1 i_2 \dots i_{n_i}, \quad (1)$$

where i_k is the k^{th} spin orbital on nucleus i . With Eq. (1) an arbitrary antisymmetrized product of n atomic spin orbitals used in the construction of the valence bond basis functions has the form

^{a)} Alfred P. Sloan Research Fellow.

$$\chi = \hat{A}_n \{ \Pi_1 \Pi_2 \dots \Pi_N \}, \quad (2)$$

where \hat{A}_n is the usual antisymmetrization operator including the normalization constant $1/\sqrt{n!}$ and " $\hat{}$ " is used to indicate an operator. For arbitrary nuclei i and j :

$$\chi = (-1)^p \hat{A}_n \{ \Pi_i \Pi_j \Pi_1 \Pi_2 \dots \Pi_{i-1} \times \Pi_{i+1} \dots \Pi_{j-1} \Pi_{j+1} \dots \Pi_N \}, \quad (3)$$

where p is the number of permutations needed to reorder the orbitals. The electrons are labeled from left to right from 1 to n . Since all possible orderings of electrons are contained in Eq. (3), χ can be rewritten as

$$\chi = (-1)^p \frac{1}{(n_i + n_j)!} \hat{A}_n \{ | \Pi_i \Pi_j | \times \Pi_1 \Pi_2 \dots \Pi_{i-1} \Pi_{i+1} \dots \Pi_{j-1} \Pi_{j+1} \dots \Pi_N \}, \quad (4)$$

where $| \dots |$ represents a determinant. This is equivalent to Eq. (3) because the $(n_i + n_j)!$ terms contained in the determinant differ only in the ordering of the electrons which does not affect the final result of the n particle antisymmetrizer. Equation (4) is of fundamental importance in this development for it shows that the antisymmetrized product of Eq. (2) can be reexpressed in terms of an antisymmetrized product that contains a determinant of spin orbitals centered on arbitrary nuclei i and j .

The DIM Hamiltonian which commutes with \hat{A}_n is expressed as

$$\hat{H} = \sum_{i>j} \hat{H}_{ij} - (N-2) \sum_{i=1}^N \hat{H}_i, \quad (5)$$

where \hat{H}_{ij} is the Hamiltonian for the isolated diatomic (ij) which operates on electrons assigned to nuclei i and j and \hat{H}_i is the corresponding atomic Hamiltonian. The diatomic valence bond eigenfunctions of \hat{H}_{ij} are expressed as linear combinations of antisymmetrized products of spin orbitals centered on i and j so that the effect of \hat{H}_{ij} on $| \Pi_i \Pi_j |$ is well defined. In fact, the result is a linear combination of determinants of spin orbitals centered on i and j with the coefficients being linear combinations of the eigenvalues of the diatomic (ij). Assuming that the functions of the form of Eq. (2) form a complete set,

$$\hat{H}_{ij} \chi_k = (-1)^{p_i} \sum_l C_{kl}^{ij} (-1)^{p_l} \chi_l, \quad (6)$$

where p_i is the number of permutations needed to reorder χ_i in the form of Eq. (3) back to the original order of the form of Eq. (2) and the coefficients, C_{kl}^{ij} are determined from the eigenvalue problem for the diatomic (ij).

Since the valence bond basis functions are linear combinations of the determinants χ_k , the effect of \hat{H}_{ij} on them is determined from Eq. (6). This gives a matrix representation of \hat{H}_{ij} in the space of the valence bond basis functions. The matrix elements depend on the eigenvalues of the diatomic (ij) and the overlaps between the determinants χ_k . Applying this procedure for each diatomic and atomic Hamiltonian in Eq. (5) leads to a matrix representation for \hat{H} in the space of the valence bond basis functions. The Hamiltonian matrix along with the valence bond overlap matrix gives the usual secular equation whose solutions furnish the needed potential surfaces.

The essential result of this section is given by Eq. (6). It leads to matrix elements of the diatomic Hamiltonians that are expressed in terms of its eigenvalues and overlaps which agree, as it should, with other formulations of this problem. In contrast to some of the other formulations, expressing the n electron antisymmetrizer as a product of a supplementary antisymmetrizer times an antisymmetrizer for electrons not on (ij) times one for the electrons on (ij) is completely avoided. Thus, functions of the form of Eq. (2) can be used directly thereby avoiding some of the transformations (or matrices) used in other formulations. Finally if \hat{H}_{ij} does not change the number of spin orbitals on either i or j , then $p = p_i$ and Eq. (6) is further simplified.

III. EXAMPLES

In this section, two examples are considered. The first consists of five equivalent nuclei with five electrons and the second consists of five equivalent nuclei with six electrons. In constructing the linearly independent set of valence bond basis spin orbitals one normally constructs the set of spin functions first. In this case, we have chosen from among the many available approaches to select spin functions using Rumer diagrams. This will not be treated in detail and the interested reader should consult Ref. 8. The set of spin functions are chosen to have common eigenvalues of \hat{S}^2 and \hat{S}_z and are then combined with the appropriate space orbitals to yield the linearly independent set of basis functions. For simplicity, only one s orbital per atom is considered.

A. Five electron case

For this system, it is assumed that four of the electrons form two bonds and the remaining electron has an α spin. This corresponds to $S = 1/2$, $M_s = 1/2$. The Rumer diagrams for this case are shown in Fig. 1. For example, the spin function θ_1 corresponding to the first Rumer diagram is given by

$$\theta_1 = 1/2 \{ [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \times [\alpha(3)\beta(4) - \beta(3)\alpha(4)] \alpha(5) \}, \quad (7)$$

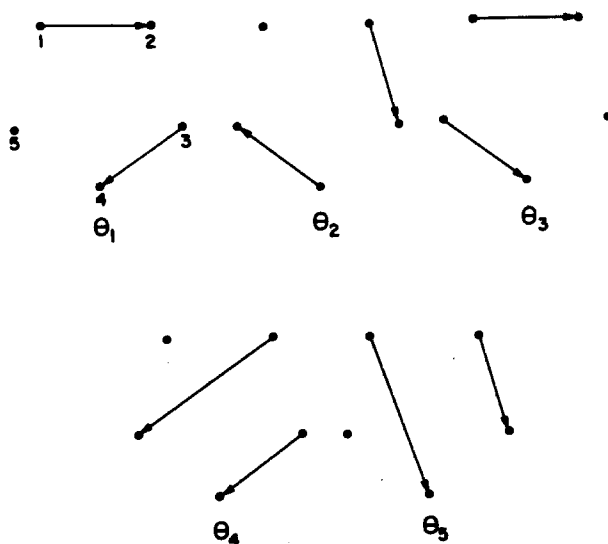


FIG. 1. Rumer diagrams for the five electron case with $S = 1/2$ and $M_s = 1/2$.

where the directed arrow going from i to j is represented as $1/\sqrt{2}[\alpha(i)\beta(j) - \beta(i)\alpha(j)]$. The spin functions in Fig. 1 form a complete set and, when combined with the appropriate atomic orbitals, form a complete basis of valence bond spin orbitals. The atomic orbitals centered on nuclei 1,2,3,4, and 5 are labeled as a,b,c,d , and e , respectively. To shorten the notation an α and β spin on orbital x is designated as x and \bar{x} , respectively. The five basis functions are then given by $[\Psi_i = \hat{A}_5\{(abcde)\theta_i\}]$:

$$\begin{aligned}\Psi_1 &= C\{\chi_1 - \chi_2 - \chi_3 + \chi_4\}, \\ \Psi_2 &= C\{\chi_1 + \chi_5 - \chi_6 - \chi_7\}, \\ \Psi_3 &= C\{\chi_1 - \chi_3 - \chi_7 + \chi_8\}, \\ \Psi_4 &= C\{-\chi_1 + \chi_2 - \chi_5 + \chi_9\}, \\ \Psi_5 &= C\{-\chi_1 - \chi_4 + \chi_6 + \chi_{10}\},\end{aligned}\quad (8)$$

where $C = 1/2\sqrt{5!}$ and the determinants χ_i are given in Table I. The basis functions Ψ_i are the same that are used in the more conventional approaches except that here we use the determinants χ_i as the fundamental entities.

The effect of the \hat{H}_{ij} 's operating on the χ_k 's is needed. The diatomic problem which is equivalent to H_2 (considering covalent structures only) is well defined, so that

$$\hat{H}_{ij}|i\bar{j}\rangle = 1/2\{(E_1^{\bar{i}} + E_2^{\bar{j}})|i\bar{j}\rangle + (E_2^{\bar{i}} - E_1^{\bar{j}})|\bar{i}j\rangle\} \quad (9)$$

and

$$\hat{H}_{ij}|ij\rangle = E_2^{\bar{i}}|ij\rangle, \quad (10)$$

where $E_1^{\bar{i}}$ ($E_2^{\bar{j}}$) corresponds to the ground (first excited) state of $(i\bar{j})$. The expression for $\hat{H}_{ij}|i\bar{j}\rangle$ is obtained by replacing i with \bar{i} and \bar{j} with j in Eq. (9) and the function $|\bar{i}j\rangle$ satisfies the same eigenvalue problem as Eq. (10). The diatomic Hamiltonians are labeled with their corresponding atomic orbitals, i.e.,

$$\begin{aligned}\hat{H} &= \hat{H}_{ab} + \hat{H}_{ac} + \hat{H}_{ad} + \hat{H}_{ae} + \hat{H}_{bc} \\ &+ \hat{H}_{bd} + \hat{H}_{be} + \hat{H}_{cd} + \hat{H}_{ce} + \hat{H}_{de} \\ &- 3(\hat{H}_a + \hat{H}_b + \hat{H}_c + \hat{H}_d + \hat{H}_e).\end{aligned}\quad (11)$$

The coefficients $C_{ki}^{\bar{j}}$ in Eq. (6) are found from Eqs. (9) and (10). Since the \hat{H}_{ij} 's do not change the number of orbitals on either i or j , $p = p_i$ so that permutations need not be considered. For example,

$$\hat{H}_{ab}\chi_1 = 1/2\{E_+^{ab}|\bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle + E_-^{ab}|\bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle\}, \quad (12)$$

where

$$E_+^{\bar{i}} = (E_1^{\bar{i}} + E_2^{\bar{i}}) \quad (13)$$

and

$$E_-^{\bar{i}} = (E_2^{\bar{i}} - E_1^{\bar{i}}). \quad (14)$$

Using Table I leads to

TABLE I. Basis determinants for the five electron system.

i	χ_i	i	χ_i
1	$ \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle$	6	$ \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle$
2	$ \bar{a}\bar{b}\bar{c}\bar{d}e\rangle$	7	$ \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle$
3	$ \bar{a}\bar{b}\bar{c}\bar{d}e\rangle$	8	$ \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle$
4	$ \bar{a}\bar{b}\bar{c}\bar{d}e\rangle$	9	$ \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle$
5	$ \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle$	10	$ \bar{a}\bar{b}\bar{c}\bar{d}\bar{e}\rangle$

$$\hat{H}_{ab}\chi_1 = 1/2\{E_+^{ab}\chi_1 + E_-^{ab}\chi_3\}. \quad (15)$$

The other results for \hat{H}_{ab} are similarly obtained and are given in Table II. Assuming that orbitals centered on different nuclei are orthogonal, the matrix elements of $\langle\Psi_i|\hat{H}_{ab}|\Psi_j\rangle$, where $\langle\dots|\dots\rangle$ represents an integration over electronic coordinates only, can be obtained. For example, using Eq. (8) and Table II results in

$$\begin{aligned}\hat{H}_{ab}\Psi_2 &= C\left\{\frac{E_+^{ab}}{2}\chi_1 + \frac{E_-^{ab}}{2}\chi_3 + E_2^{ab}\chi_5\right. \\ &\left.- E_2^{ab}\chi_6 - \frac{E_+^{ab}}{2}\chi_7 - \frac{E_-^{ab}}{2}\chi_8\right\}.\end{aligned}\quad (16)$$

Then from Eqs. (8), (13), and (14),

$$\langle\Psi_1|\hat{H}_{ab}|\Psi_2\rangle = 1/4 E_1^{ab}, \quad (17)$$

where $\langle\Psi_1|\Psi_2\rangle = 1/4$. The determination of other matrix elements $\langle\Psi_k|\hat{H}_{ij}|\Psi_l\rangle$ follows in an analogous manner.

B. Six electron case

In this case, there are six electrons distributed among five equivalent nuclei. Since each nucleus has one s -atomic orbital, one of the nuclear orbitals must be doubly occupied. The Rumer diagrams for the six electron case are shown in Fig. 2 for the case $S = 0$, $M_s = 0$. The actual spin functions can be determined in the same way as in the previous example. Since there are five nuclei, there are five orbital configurations to be considered and they are given by, in the notation of the previous example, $abcde$, $abbcd$, $abccde$, $abccde$, and $abcdee$. These are then combined with the appropriate spin functions. For example, in the configuration $abcde$, electrons 1 and 2 are paired so that this configuration is combined with either θ_1 or θ_3 . By analogous arguments, $abbcd$ is combined with θ_2 or θ_5 , and so on. Carrying through this procedure results in the set of basis functions given in Table III with the determinants χ_i^α defined in Table IV. The superscript " α " in χ_i^α designates which nucleus is doubly occupied.

As in the previous example, the next step involves determining the effect of the \hat{H}_{ij} 's on the χ_i^α 's. There are two diatomic problems that need to be considered. The first consists of a diatomic $(i\bar{j})$ in which each nucleus is assigned one electron as was illustrated in the previous example in Eqs. (9) and (10). The second case for the diatomic $(i\bar{j})$ consists of say two electrons on nucleus i and one on j . This corresponds, for

TABLE II. Effect of the operation of \hat{H}_{ab} on χ_i .

i	Right-hand side of Eq. (6)
1	$1/2(E_+^{ab}\chi_1 + E_-^{ab}\chi_3)$
2	$1/2(E_+^{ab}\chi_2 + E_-^{ab}\chi_4)$
3	$1/2(E_+^{ab}\chi_3 + E_-^{ab}\chi_1)$
4	$1/2(E_+^{ab}\chi_4 + E_-^{ab}\chi_2)$
5	$E_2^{ab}\chi_5$
6	$E_2^{ab}\chi_6$
7	$1/2(E_+^{ab}\chi_7 + E_-^{ab}\chi_8)$
8	$1/2(E_+^{ab}\chi_8 + E_-^{ab}\chi_7)$
9	$E_2^{ab}\chi_9$
10	$E_2^{ab}\chi_{10}$

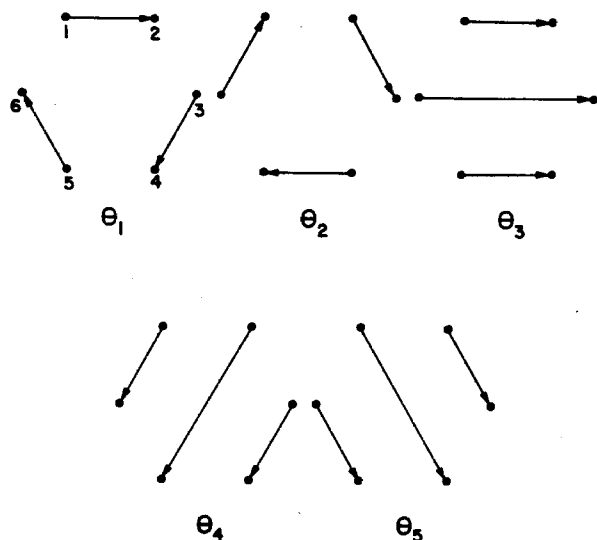


FIG. 2. Rumer diagrams for the six electron case with $S = 0$ and $M_s = 0$.

$M_{s_{ij}} = 1/2$, to a valence bond function of the form $|i\bar{i}j\bar{j}| - |\bar{i}ijj|$. Similarly if two electrons are on j and one on i , then the valence bond function has the form $|ijj\bar{j}| - |\bar{i}j\bar{j}j|$. Assuming that the ground state is the sum of these functions and the excited state is their difference:

$$\Psi_1^j = C \{ |i\bar{i}j\bar{j}| - |\bar{i}ijj| + |ijj\bar{j}| - |\bar{i}j\bar{j}j| \} \quad (18)$$

and

$$\Psi_2^j = C \{ |i\bar{i}j\bar{j}| - |\bar{i}ijj| - |ijj\bar{j}| + |i\bar{j}j\bar{j}| \}, \quad (19)$$

where

$$\hat{H}_{ij} \Psi_k^j = E_k^j \Psi_k^j, \quad (20)$$

$k = 1, 2$, and $E_1^j < E_2^j$. It follows from these relations that

$$\hat{H}_{ij} |i\bar{i}j\bar{j}| = 1/2 \{ (E_1^j + E_2^j) |i\bar{i}j\bar{j}| + (E_1^j - E_2^j) |i\bar{j}j\bar{j}| \}. \quad (21)$$

Similar results are obtained for the $M_{s_{ij}} = -1/2$ case.

From the above results we can determine the effect of the \hat{H}_{ij} 's on the Ψ_i 's. As typical example, expressions for $\hat{H}_{bc} \Psi_1$ and $\hat{H}_{ae} \Psi_1$ are obtained. As in the previous example, \hat{H}_{bc} does not change the number of orbitals on either b or c in Ψ_1 so that $p = p_l$ for all l in Eq. (6). Then from Eqs. (6), (9), and (10) and Tables III and IV:

TABLE III. Valence bond basis functions for the six electron, five nuclei system. The normalization constant N is $(2\sqrt{6})^{-1}$. The determinants are given in Table IV.

i	Ψ_i
1	$N(\chi_1^2 - \chi_2^2 - \chi_3^2 + \chi_4^2)$
2	$N(-\chi_1^2 - \chi_4^2 + \chi_5^2 + \chi_6^2)$
3	$N(\chi_1^2 - \chi_2^2 - \chi_3^2 + \chi_4^2)$
4	$N(-\chi_1^2 - \chi_4^2 + \chi_5^2 + \chi_6^2)$
5	$N(\chi_1^2 - \chi_2^2 - \chi_3^2 + \chi_4^2)$
6	$N(-\chi_1^2 - \chi_4^2 + \chi_5^2 + \chi_6^2)$
7	$N(\chi_1^2 - \chi_2^2 - \chi_3^2 + \chi_4^2)$
8	$N(\chi_1^2 + \chi_4^2 - \chi_5^2 - \chi_6^2)$
9	$N(\chi_1^2 - \chi_2^2 - \chi_3^2 + \chi_4^2)$
10	$N(\chi_1^2 + \chi_4^2 - \chi_5^2 - \chi_6^2)$

TABLE IV. Basis determinants for the six electron case.

χ_i^a	$a =$	a	b	c	d	e
1		$ a\bar{a}b\bar{c}d\bar{e} $	$ \bar{a}b\bar{b}c\bar{d}e $	$ \bar{a}b\bar{c}c\bar{d}\bar{e} $	$ \bar{a}b\bar{c}d\bar{d}e $	$ \bar{a}b\bar{c}d\bar{e}e $
2		$ a\bar{a}b\bar{c}d\bar{e} $	$ abb\bar{c}d\bar{e} $	$ abc\bar{c}d\bar{e} $	$ ab\bar{c}d\bar{d}e $	$ ab\bar{c}d\bar{e}e $
3		$ a\bar{a}b\bar{c}d\bar{e} $	$ \bar{a}b\bar{b}c\bar{d}e $	$ \bar{a}b\bar{c}c\bar{d}\bar{e} $	$ \bar{a}b\bar{c}d\bar{d}e $	$ \bar{a}b\bar{c}d\bar{e}e $
4		$ a\bar{a}b\bar{c}d\bar{e} $	$ abb\bar{c}d\bar{e} $	$ \bar{a}b\bar{c}c\bar{d}\bar{e} $	$ ab\bar{c}d\bar{d}e $	$ \bar{a}b\bar{c}d\bar{e}e $
5		$ a\bar{a}b\bar{c}d\bar{e} $	$ \bar{a}b\bar{b}c\bar{d}e $	$ \bar{a}b\bar{c}c\bar{d}\bar{e} $	$ \bar{a}b\bar{c}d\bar{d}e $	$ \bar{a}b\bar{c}d\bar{e}e $
6		$ a\bar{a}b\bar{c}d\bar{e} $	$ \bar{a}b\bar{b}c\bar{d}e $	$ \bar{a}b\bar{c}c\bar{d}\bar{e} $	$ \bar{a}b\bar{c}d\bar{d}e $	$ \bar{a}b\bar{c}d\bar{e}e $

$$\hat{H}_{bc} \Psi_1 = \frac{N}{2} \{ E_+^{bc} \chi_1^a + E_-^{bc} \chi_3^a - E_+^{bc} \chi_2^a - E_-^{bc} \chi_4^a - E_+^{bc} \chi_5^a - E_-^{bc} \chi_6^a + E_+^{bc} \chi_7^a + E_-^{bc} \chi_9^a \}. \quad (22)$$

Collecting terms and using Eqs. (13) and (14) results in

$$\hat{H}_{bc} \Psi_1 = E_1^{bc} \Psi_1, \quad (23)$$

which is what one would expect since Ψ_1 contains a bc bond.

The final case of determining $\hat{H}_{ae} \Psi_1$ should help clarify why it is necessary to keep track of the number of permutations needed to go from Eq. (2) to Eq. (3) and then back to Eq. (2). For example, note that $|a\bar{a}b\bar{c}d\bar{e}| = -|a\bar{a}e\bar{b}c\bar{d}|$. From Eq. (21), one obtains the determinant $|a\bar{e}e\bar{b}c\bar{d}|$ which when the proper order is restored results in $+|a\bar{b}c\bar{d}e|$. Determinants in Eq. (6) that contain two "a" orbitals are preceded by a factor of (+1) whereas those that have two "e" orbitals are multiplied by a factor of (-1). Then from Eqs. (6) and (21) and Tables III and IV

$$\hat{H}_{ae} \Psi_1 = \frac{N}{2} \{ (E_1^{ae} + E_2^{ae}) \chi_1^a + (-1)(E_1^{ae} - E_2^{ae}) \chi_2^a - (E_1^{ae} + E_2^{ae}) \chi_3^a - (-1)(E_1^{ae} - E_2^{ae}) \chi_4^a - (E_1^{ae} + E_2^{ae}) \chi_5^a - (-1)(E_1^{ae} - E_2^{ae}) \chi_6^a + (E_1^{ae} + E_2^{ae}) \chi_7^a + (-1)(E_1^{ae} - E_2^{ae}) \chi_8^a \}. \quad (24)$$

Using Table III results in

$$\hat{H}_{ae} \Psi_1 = 1/2 \{ (E_1^{ae} + E_2^{ae}) \Psi_1 - (E_1^{ae} - E_2^{ae}) \Psi_{10} \}. \quad (25)$$

Assuming that

$$\langle \chi_i^a | \chi_j^b \rangle = \delta_{ij} \delta_{ab}, \quad (26)$$

then it is simple to determine $\langle \Psi_1 | \hat{H}_{ij} | \Psi_1 \rangle$. General terms of the form $\langle \Psi_i | \hat{H}_{ij} | \Psi_k \rangle$ are obtained in an equivalent fashion.

IV. CLOSING REMARKS

The examples provided in the previous section provide an illustration of how to apply the formalism developed in Sec. II. The use of a matrix formalism was purposefully avoided in order to add clarity and to emphasize the simplicity of this procedure. It is, however, straightforward to develop this approach in terms of matrix notation. Letting

$$\Psi_i = \sum_{j=1}^l b_{ji} \chi_j \quad (27)$$

and

$$\Psi = (|\Psi_1\rangle|\Psi_2\rangle\dots|\Psi_m\rangle) = \chi\mathbf{b}, \quad (28)$$

where

$$\chi = (|\chi_1\rangle|\chi_2\rangle\dots|\chi_l\rangle) \quad (29)$$

and \mathbf{b} is an $(l \times m)$ rectangular matrix, then

$$\Psi^\dagger \hat{H}_{ij} \Psi = \mathbf{b}^\dagger \chi^\dagger \hat{H}_{ij} \chi \mathbf{b}, \quad (30)$$

where

$$\psi^\dagger = \begin{pmatrix} \langle \Psi_1 | \\ \langle \Psi_2 | \\ \vdots \\ \langle \Psi_m | \end{pmatrix}. \quad (31)$$

An analogous definition holds for χ^\dagger . Equation (30) is the matrix representation of \hat{H}_{ij} in the basis of the valence bond functions. The general prescription for constructing these matrices is: (1) determine the basis set of valence bond functions. This gives the matrices $\chi(\chi^\dagger)$ and $\mathbf{b}(\mathbf{b}^\dagger)$. (2) Define the eigenvalue problem for all diatomic and atomic components. (3) Construct the matrix representation of each Hamiltonian (\hat{H}_{ij} and \hat{H}_i) in the χ representation via Eq. (6). (4) Add the matrices together as in Eq. (5) which gives the matrix representation of \hat{H} in the space of χ . (5) Multiply this matrix on the right and left by \mathbf{b} and \mathbf{b}^\dagger , respectively. This matrix along with the valence bond overlap matrix are the ones needed in the secular equation.

It is somewhat instructive to qualitatively compare our approach with the ones based on partitioning the antisymmetrizer. From Eqs. (5), (6), and (27), the effect of a diatomic Hamiltonian on a valence bond wave function is

$$\hat{H}_{ij} \Psi_m = \sum_k b_{km} \sum_l (-1) C_{kl}^{ij} \chi_l, \quad (32)$$

where $p_k + p_l$ is the number of permutations necessary to reorder χ_k from the form of Eq. (2) to the form of Eq. (3). The corresponding expression from Ellison's treatment [Eq. (25) in Ref. 1] is

$$\hat{H}_{ij} \Psi_m = \sum_s E_s^{ij} \sum_u g_{su} \chi_u. \quad (33)$$

This expression is somewhat appealing since the diatomic eigenvalues enter the expression directly but the evaluation of the coefficients g_{su} is far from trivial and normally requires a considerable amount of bookkeeping [see Eqs. (18) to (25) in Ref. 1]. In contrast, the evaluation of the quantities appearing in Eq. (32) is much more direct. The expansion coefficients, b_{km} are known from the outset, determining the p_l and p_k even for systems with many electrons is trivial, and

the coefficients C_{kl}^{ij} are determined from the eigenvalue problem for the diatomic (ij). The only difficulty in evaluating Eq. (32) is in knowing which determinants χ_l are generated from \hat{H}_{ij} operating on χ_k . As demonstrated in the examples, this poses no great problem.

This approach to the DIM procedure is equivalent to other formulations. That is, identical input information produces the same final polyatomic surface. In addition, the procedure presented here can be expanded analogous to what is done in other formulations. Spin-orbit interactions can be included by appropriately modifying the atomic and diatomic Hamiltonians. Naturally an expanded basis set that includes the atomic states with the spin-orbit coupling must be used. Directional bonding can be included in a manner similar to that given in Ref. 3. Matrix elements of the adiabatic coupling vector can be determined so that transitions between states due to the breakdown of the Born-Oppenheimer approximation can be described. As with other approaches, difficulty arises when there are two or more diatomic states of the same symmetry. The coupling between the states must be known.

In conclusion, it is hoped that this paper has provided a straightforward approach to calculating potential energy surfaces with the DIM method. The examples point out that this approach can be formally applied to rather complicated systems and thus has the capability for describing interaction potentials between a surface and an adsorbed or colliding particle. Work on these problems is currently underway.

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