Triatomics-in-molecules method applied to helium cluster cations

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ABSTRACT
The triatomics-in-molecules (TRIM) method for calculating potential energy surfaces (PES) is discussed. The method is a modification of Ellison's diatomics-in-molecules (DIM) approach (F. O. ELLISON, F.O. J. Am. Chem. Soc. 1963, vol. 85, p. 3540) and consists in expanding the electronic hamiltonian of a polyatomic system into terms corresponding to the three- and monoatomic fragments. Application of the general theory to a special case of the \( \text{He}_n^+ \) clusters is presented.

KEY WORDS
diatomics-in-molecule; triatomics-in-molecules; helium; cluster cations
1. INTRODUCTION

Since publication of the original paper by Ellison [1], the diatomics-in-molecules (DIM) method has been successfully used in a series of calculations of electronic and geometrical structure of molecules and clusters. In particular, it has proved very useful if applied to the singly positively charged rare gas clusters, $Rg_n^+$ [2]. Electronic structures, equilibrium geometries, photoabsorption spectra, and collision dynamics of rare-gas cations have been studied extensively using the semi-empirical DIM surfaces. The only exceptions are the $He_n^+$ clusters, for which the DIM approach fails completely [3]. This is mainly due to non-negligible three-body effects, which are not taken into account within the minimal DIM approach [4]. Even for the heavier rare gases (neon - xenon), for which the minimal DIM approach is fairly accurate, the many-body contributions to the interaction energy are to be considered in accurate calculations. At least the leading, induced dipole - induced dipole three-body interaction term is to be taken into account [5].

In this work a modification of the standard DIM method [1] is proposed which explicitly includes all the three-body interaction terms into molecular electronic hamiltonian. First, the general theory is developed in Section 2, following by part a prior work by Wu [6], then the theory is applied to a special case of the $He_n^+$ cations in Section 3.

2. THEORY

Similarly to the Ellison's DIM approach [1] and following the more general theory by Wu [6], the present method consists in assigning each electron to a particular atom and partitioning the electronic hamiltonian of a polyatomic system into three- and monoatomic terms. This is done in the following way. The total Hamiltonian operator $\hat{H}$ can be written as a sum of the monoatomic hamiltonians and the remaining two-atomic interaction terms

$$\hat{H} = \sum_p \hat{H}_p + \sum_{p,o} \hat{V}_{pq},$$

(1)
where each atomic hamiltonian, \( \hat{H}_P \), consists of the total kinetic energy of the electrons assigned to atom \( P \) and of the terms corresponding to the interactions of these electrons with nucleus \( P \) and between different pairs of the electrons belonging to atom \( P \), whereas the interaction operators, \( \hat{V}_{PQ} \), include the terms representing the interactions of the electrons originally assigned to atom \( P \) with nucleus \( Q \) and \textit{vice versa}. In particular, the three-atomic hamiltonian corresponding to the \( PQR \) triatom can be written as follows

\[
\hat{H}_{PQR} = \hat{H}_P + \hat{H}_Q + \hat{H}_R + \hat{V}_{PQ} + \hat{V}_{QR} + \hat{V}_{PR}.
\]  

(2)

Summing over the indices \( P, Q, \) and \( R \) yields in this formula

\[
\sum_{R>Q>P} \hat{H}_{PQR} = 3(N-1)(N-2)\sum_P \hat{H}_P + 3(N-1)\sum_{Q>P} \hat{V}_{PQ},
\]  

(3)

where \( N \) denotes the total number of atoms in the molecule. If Eq. (3) is solved for \( \sum V_{PQ} \) and the result inserted into Eq. (1), we get

\[
\hat{H} = \frac{1}{3(N-1)} \sum_{R>Q>P} \hat{H}_{PQR} - (N-3)\sum_P \hat{H}_P.
\]  

(4)

Thus, the total Hamiltonian operator is written as a sum of three- and monoatomic operators. Eq. (4) is usually called the \textit{triatomics-in-molecule} (TRIM) expansion of the overall hamiltonian \( \hat{H} \).

Clearly, the above procedure can be generalized and the total Hamiltonian operator can be expressed in terms of mono- and K-atomic (\( K < N \)) fragments,

\[
\hat{H} = \frac{1}{K(K-1)} \frac{(N-K)!}{(N-2)!} \sum_{R_1 > \cdots > R_K} \hat{H}_{R_1 \cdots R_K} - \frac{(N-K)}{(K-1)} \sum_P \hat{H}_P.
\]  

(5)

Expansion (5) is not much practical, however, because the larger \( K \)-atomic fragments are considered the more consuming preliminary calculations are needed to get all the necessary \( K\)-
atomic inputs. In addition, huge technical difficulties regarding appropriate analytical representation of K-particle interaction energies will appear if K is larger than 3.

Let now proceed to the evaluation of the Hamiltonian matrix elements in a particular electronic wave-function basis. At this stage of development, the procedure originally proposed by Ellison [1] can be followed immediately. Let $\Psi_n^*$ and $\Phi_n$ denote the antisymmetrized and non-antisymmetrized electronic wave functions, respectively,

$$\Psi_n = \hat{A}\Phi_n,$$  \hspace{1cm} (6)

where $\hat{A}$ is the total antisymmetrization operator. Then, since the antisymmetrization operator $\hat{A}$ commutes with the total Hamiltonian $\hat{H}$, it can be written for the corresponding Hamiltonian matrix

$$H_{mn} \equiv \langle \Psi_m \mid \hat{H}\Psi_n \rangle = \langle \Psi_m \mid \hat{H}\hat{A}\Phi_n \rangle = \langle \Psi_m \mid \hat{A}\hat{H}\Phi_n \rangle.$$  \hspace{1cm} (7)

As usually, symbol $\langle \mid \rangle$ denotes integration over the positions of all the electrons, $\langle \varphi \mid \psi \rangle = \int \varphi^* \psi \, d\Gamma$, the asterisk indicating the complex conjugation. The total Hamiltonian matrix can further be expressed in terms of three- and monoatomic fragments (cf. Eq. 4)

$$H_{mn} = \frac{1}{3(N-1)} \sum_{R\neq Q\neq P} H_{mn}^{PQR} - (N-3)\sum_p H_{mn}^p$$  \hspace{1cm} (8)

with $H_{mn}^{PQR} = \langle \Psi_m \mid \hat{A}\hat{H}_{PQR}\Phi_n \rangle$ and $H_{mn}^p = \langle \Psi_m \mid \hat{A}\hat{H}_{P}\Phi_n \rangle$. If a decomposition of the antisymmetrization operator, similar to that employed by Ellison [1], is used,

$$\hat{A} = \hat{A}^{(PQR)}_{PQR} \hat{A}^{(P)}_P \hat{A}^{(Q)}_Q \hat{A}^{(R)}_R,$$  \hspace{1cm} (9)
with \( \hat{A}_{\text{PQR}} \) antisymmetrizing over all the electrons belonging to the \( PQR \) triatom, \( \hat{A}^{(\text{PQR})} \) over those belonging to the remainder of the molecule, and \( \hat{A}_{\text{PQR}}^{(\text{PQR})} \) containing all the remaining antisymmetrizations, the following holds

\[
\hat{A}\hat{H}_{\text{PQR}}\Phi_n = \hat{A}^{(\text{PQR})}\hat{H}_{\text{PQR}}\hat{A}^{(\text{PQR})}\hat{A}_{\text{PQR}}\Phi_n = \hat{A}^{(\text{PQR})}\hat{H}_{\text{PQR}}\Psi_{\text{PQR}}^{\text{PQR}}\Psi_{\text{PQR}}^{(\text{PQR})},
\]

(10)

for both \( \hat{A}^{(\text{PQR})} \) and \( \hat{A}_{\text{PQR}}^{(\text{PQR})} \) commute with the triatomic hamiltonian \( \hat{H}_{\text{PQR}} \). In Eq. (10) \( \Psi_{\text{PQR}}^{\text{PQR}} \) and \( \Psi_{\text{PQR}}^{(\text{PQR})} \) denote the antisymmetrized electronic wave functions of the \( PQR \) fragment and the remainder of the molecule, respectively, corresponding to \( \Psi_n \). Provided \( \Psi_{\text{PQR}}^{\text{PQR}} \) can be written as a linear combination of the eigenvectors of the triatomic hamiltonian \( \hat{H}_{\text{PQR}} \),

\[
\Psi_{\text{PQR}}^{\text{PQR}} = \sum_j n_{\text{PQR},j}^n \psi_{\text{PQR}}^{\text{PQR}}
\]

(11)

with \( \hat{H}_{\text{PQR}}\psi_{\text{PQR}}^{\text{PQR}} = E_{\text{PQR}}^{\text{PQR}}\psi_{\text{PQR}}^{\text{PQR}} \), \( E_{\text{PQR}}^{\text{PQR}} \) being the corresponding eigenvalues, and if Eq. (11) can be uniquely inverted,

\[
\psi_{\text{PQR}}^{\text{PQR}} = \sum_n \xi_{\text{PQR},n} n_{\text{PQR}}^n \psi_{\text{PQR}}^{\text{PQR}}
\]

(12)

then the following holds

\[
\hat{H}_{\text{PQR}}\Psi_{\text{PQR}}^{\text{PQR}} = \sum_j n_{\text{PQR},j}^n E_{\text{PQR}}^{\text{PQR}}\psi_{\text{PQR}}^{\text{PQR}} = \sum_k \left( \sum_j n_{\text{PQR},j}^n \xi_{\text{PQR},j,k} \right) E_{\text{PQR}}^{\text{PQR}}\Psi_{\text{PQR}}^{\text{PQR}}
\]

(13)

and accordingly

\[
\hat{A}^{(\text{PQR})}\hat{H}_{\text{PQR}}\Psi_{\text{PQR}}^{\text{PQR}}\Psi_{\text{PQR}}^{(\text{PQR})} = \sum_k \left( \sum_j n_{\text{PQR},j}^n \xi_{\text{PQR},j,k} E_{\text{PQR}}^{\text{PQR}} \right) \hat{A}^{(\text{PQR})}\Psi_{\text{PQR}}^{\text{PQR}}\Psi_{\text{PQR}}^{(\text{PQR})}
\]

(14)
Next, if the basis wave functions $\Psi_m$ are chosen properly so that, for each choice of indices $k$ and $n$,

$$\hat{A}_{PQR}^{(PQR)} \Psi_k^{(PQR)} \Psi_n^{(PQR)}$$

is also a basis wave function, than the following holds

$$\hat{A} \hat{H}_{PQR} \Phi_p = \sum_p \left( \sum_j \eta_{n,j}^{PQR} \xi_{j,k}^{PQR} E_j^{PQR} \right) \Psi_p ,$$

(15)

where the first sum runs over all the indices $p$ for which $\Psi_p = \hat{A}_{PQR}^{(PQR)} \Psi_k^{(PQR)} \Psi_n^{(PQR)}$ for the particular choice of $k$ and $n$. Consequently, the corresponding matrix elements, $H_{mn}^{PQR} = \langle \Psi_m | \hat{A} \hat{H}_{PQR} | \Phi_n \rangle$, read as follows

$$H_{mn}^{PQR} = \sum_p \left( \sum_j \eta_{n,j}^{PQR} \xi_{j,k}^{PQR} E_j^{PQR} \right) \langle \Psi_m | \Psi_p \rangle .$$

(16)

The matrix elements of the atomic hamiltonians, $H_{mn}^P$, can be evaluated in a similar way. The expressions are not given here explicitly, however, for they may be neglected if the dissociation limit is chosen properly. (See also Sec. 3.)

3. APPLICATION TO THE HELIUM CLUSTER CATIONS

With all the three-body interactions included, we believe in accordance with other authors the minimal DIM basis [4] will work for helium. Thus, we choose the basis wave functions $\Psi_n$ in the form of normalized Slater determinants with the positive hole localized on one of the helium atoms:

$$\Psi_1 = \left| a_1 a_2 \bar{a}_2 ... a_N \bar{a}_N \right|,$$

$$\Psi_2 = \left| a_1 \bar{a}_2 a_2 ... a_N \bar{a}_N \right|,$$

$$\ldots$$

$$\Psi_N = \left| a_1 \bar{a}_1 a_2 \bar{a}_2 ... a_N \right|,$$

(17)
where \( a_K \) denotes a 1s orbital localized on atom \( K \) occupied by an electron having the \( z \)-component of spin equal +1/2 and the stripe corresponds to the \( z \)-component of spin equal to -1/2. Since the spin-sensitive interactions are not significant in helium, additional wave functions

\[
\Psi_1 = |\bar{a}_1, \bar{a}_2, \ldots, \bar{a}_N| \quad \text{etc. need not be considered.}
\]

The ground state of a neutral \( PQR \) triatom is approximated by a normalized Slater-type wave function

\[
\psi^{PQR} = |a_P \bar{a}_P a_Q \bar{a}_Q a_R \bar{a}_R|.
\] (18)

For a particular ionic \( PQR \) triatom, the following basis wave functions are employed

\[
\psi_{PQR}^1 = |a_P a_Q a_R \bar{a}_R|,
\]

\[
\psi_{PQR}^2 = |a_P \bar{a}_P a_Q a_R|,
\]

\[
\psi_{PQR}^3 = |a_P a_Q a_R \bar{a}_R|,
\] (19)

ionic character of the fragment being indicated by small letters used in the upper indices.

If all of this is taken into account, the total Hamiltonian matrix can be written, employing the general procedure described in Sec. 2, as a sum of triatomic contributions

\[
H_{nn} = \frac{1}{3(N-1)} \sum_{R>Q>P} H_{nn}^{PQR},
\] (20)

where the triatomic matrices read as follows

\[
H_{nn}^{PQR} = E_{nn}^{PQR}, \quad \text{for } m \neq P, Q, R,
\]

\[
H_{nn}^{PQR} = \sum_{k=1}^{3} \eta_{j,k}^{PQR} \xi_{k,j}^{PQR} E_{kk}^{PQR},
\] (21)

*Here, zero of the total energy of a \( He_{n+} \) cluster corresponds to the dissociated state, \( He^+ + (n-1) He \), and the atomic energies may thus be neglected.*
with \( j = 1, 2, 3 \) for \( m = P, Q, R \), respectively, and \( l = 1, 2, 3 \) for \( n = P, Q, R \), respectively, and

\[
H_{mn}^{\text{PQR}} = 0
\]  

elsewhere. Since overlap effects are not important in \( He_n^+ \) clusters [7], the overlap integrals, \( \langle \Psi_K | \Psi_L \rangle \), are neglected for \( K \neq L \).

In Eq. (21), \( E_{\text{PQR}}^{\text{PQR}} \) denotes the ground state energy of a neutral \( PQR \) fragment, and \( E_1^{\text{PQR}} \leq E_2^{\text{PQR}} \leq E_3^{\text{PQR}} \) are energies corresponding to the ground state and the first two excited states of an ionic \( PQR \) fragment. The expansion coefficients \( \eta_{j,k}^{\text{PQR}} \) and \( \xi_{k,j}^{\text{PQR}} \) have the same meaning as discussed in Sec. 2. Thus, the latter coefficients are obtained by solving the characteristic equation for the ionic \( PQR \) fragment

\[
\sum_{j=1}^{3} \left( \langle \psi_i^{\text{PQR}} | \hat{H}^{\text{PQR}} | \psi_j^{\text{PQR}} \rangle - E_k^{\text{PQR}} \langle \psi_i^{\text{PQR}} | \psi_j^{\text{PQR}} \rangle \right) \xi_{j,k}^{\text{PQR}} = 0, 
\]  

\( \hat{H}^{\text{PQR}} \) being the Hamiltonian operator for the \( PQR \) fragment, whereas the \( \eta_{j,k}^{\text{PQR}} \) coefficients can be obtained from a completeness relation

\[
\sum_{j=1}^{3} \xi_{k,j}^{\text{PQR}} \eta_{j,k}^{\text{PQR}} = \delta_{kl}, 
\]  

\( \delta_{kl} \) is the Kronecker delta, which follows from Eqs. (11) and (12). Again, the overlap integrals may be neglected in Eq. (23), \( \langle \psi_i^{\text{PQR}} | \psi_j^{\text{PQR}} \rangle \approx \delta_{ij} \). In contrast to the standard DIM method, the values of both \( \xi \) and \( \eta \) expansion coefficients will depend on the particular configuration of the nuclei.
4. CONCLUSIONS

The TRIM method for calculating potential energy surfaces has been discussed in detail and applied to helium cluster cations. For the method to be employed successfully in calculations, accurate input data on the interactions in all the triatoms, into which the polyatomic system is fragmented, must be available. These triatomic inputs are to be supplied from highly accurate \textit{ab initio} calculations. In the special case of helium clusters, the necessary triatomic input includes primarily three potential energy surfaces for the ground state and the first two excited electronic states in helium trimer cation, $\text{He}_3^+$. At present, extensive \textit{ab initio} calculations are in preparation to obtain these surfaces [8].

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