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Variational Scheme for Multistate Kets

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A scheme is proposed in which a multistate ket is variationally computed, subject to certain symmetry constraints. Computational characteristics of the method, including the recovery of single-state kets and energies, and the avoidance of three-center and four-center molecular integrals, are discussed.

I. INTRODUCTION

Kets employed in *ab initio* molecular calculations are often symmetry-adapted to the group of the Hamiltonian. As is well known, such a scheme factors the secular equation into blocks. Here we propose an alternative method which involves variationally computing a nonsymmetrized multistate ket, subject to certain symmetry constraints. The method yields energies and individual-state kets arising from a given separated-atom limit and is formulated in terms of a limited configuration-interaction basis; as the basis becomes complete, the scheme yields exact results.

Since the multistate ket is not symmetry-adapted to the symmetric group $\mathcal{S}_N$ of permutations on the N electronic indices, Hamiltonian matrix elements over the multistate ket need not involve three- or four-center molecular integrals. Although the multistate ket is not symmetry-adapted to $\mathcal{S}_N$, one may desire to symmetry-adapt it to a subgroup of $\mathcal{S}_N$. If this subgroup of $\mathcal{S}_N$ is chosen to be $\mathcal{S}^0$, the maximal set of permutations which transfer no electrons among different atoms, then three- and four-center integrals still need not arise. This subgroup $\mathcal{S}^0 \subseteq \mathcal{S}_N$ is given as

$$\mathcal{S}^0 = \mathcal{S}_A \otimes \mathcal{S}_B \otimes \mathcal{S}_C \otimes \cdots \quad , \tag{1.1}$$

if $\mathcal{S}_A, \mathcal{S}_B, \ldots$ are the symmetric groups for different sets of electrons assigned to atoms $A, B, \ldots$. The present scheme using a spin-free Hamiltonian is conveniently described in a spin-free formulation[1,2] employing the algebraic theory and notation of previous papers.[3-5]

The variationally obtained multistate ket is similar to that arising in a generalization[4] of the Hirschfelder-Silbey perturbation theory.[6] Indeed, they become identical with unlimited configuration interaction. The use of the constrained variational principle here differs from previous applications[7] which have constrained expectation values of dynamically determined molecular properties over a single-state ket.

II. FORMULATION OF THE PROBLEM

Solutions to a spin-free Hamiltonian H are to be obtained in the νth approximation employing a spin-free vector space $\mathfrak{U}^\nu$. The space $\mathfrak{U}^\nu$ is assumed to have a basis

$$\{|K^0;\, \alpha^0 r^0\rangle;\ K^0 \text{ ranging}\} \tag{2.1}$$

such that every basis ket transforms at the r^0th column of the α^0th irreducible representation (IR) of $\mathcal{S}^0$. Thus for any $P^0 \in \mathcal{S}^0$,

$$P^0 |K^0;\, \alpha^0 r^0\rangle = \sum_{s^0} [P^0]^{\alpha^0}_{s^0 r^0} |K^0;\, \alpha^0 s^0\rangle \ , \tag{2.2}$$

where $[P^0]^{\alpha^0}_{s^0 r^0}$ is the $s^0 r^0$th matrix element of the α^0th IR of the permutation P^0. Recalling (1.1) we see that α^0 of $\mathcal{S}^0$ is a Kronecker product of IR $\alpha_A, \alpha_B, \ldots$ for $\mathcal{S}_A, \mathcal{S}_B, \ldots$:

$$\alpha^0 = \alpha_A \otimes \alpha_B \otimes \cdots \ , \tag{2.3}$$

$$r^0 = r_A \quad r_B \otimes \cdots \ . \tag{2.4}$$

The basis (2.1) for $\mathfrak{U}^\nu$ might conveniently be chosen as product kets

$$|K^0;\, \alpha^0 r^0\rangle = |K_A;\, \alpha_A r_A\rangle \otimes |K_B;\, \alpha_B r_B\rangle \otimes \cdots \ , \tag{2.5}$$

where $|K_A;\, \alpha_A r_A\rangle$, $|K_B;\, \alpha_B r_B\rangle, \ldots$ are many-electron kets symmetry-adapted to $\mathcal{S}_A, \mathcal{S}_B, \ldots$ and centered on atoms $A, B, \ldots$ However, the basis of $\mathfrak{U}^\nu$ need not necessarily be of this simple product form for the formal equations developed here to still apply.

Matric basis elements for $\mathcal{S}_N$ which are *sequence-adapted*[3,5] to $\mathcal{S}^0 \subseteq \mathcal{S}_N$ will be useful; they may be given as

$$e^\alpha_{(\rho\alpha^0 r^0)(\sigma\beta^0 s^0)} = \frac{f^\alpha}{N!} \sum_{P \in \mathcal{S}_N} [P^{-1}]^\alpha_{(\sigma\beta^0 s^0)(\rho\alpha^0 r^0)} P \ . \tag{2.6}$$

Here $[P^{-1}]^\alpha_{(\sigma\beta^0 s^0)(\rho\alpha^0 r^0)}$ is the $(\sigma\beta^0 s^0)(\rho\alpha^0 r^0)$th matrix element of the f^α-dimensional αth IR of P^{-1}. The symbols ρ and σ distinguish rows or columns of the matrix representation of P^{-1} when the labels $\alpha^0 r^0$ and $\beta^0 s^0$ are not sufficient; ρ and σ take on values equal in number to the frequency $f^{\alpha^0 \uparrow \alpha}$ of the αth IR of $\mathcal{S}_N$ in the representation *induced* from α^0 of $\mathcal{S}^0$. Since the sequence-adapted IR matrix elements of permutations $P^0 \in \mathcal{S}^0$ are block diagonal

$$[P^0]^{\alpha}_{(\sigma\beta^0 s^0)\,(\rho\alpha^0 r^0)} = \delta_{\rho\sigma}\delta_{\alpha^0\beta^0}[P^0]^{\alpha^0}_{s^0 r^0} , \tag{2.7}$$

the matrix basis element (2.6) transforms on the left as $\alpha^0 r^0$ of $\mathcal{S}^0$ and on the right as $B^0 s^0$.

Conventionally, approximations to the eigenvalues and eigenkets of H are obtained by inducing the space $\mathfrak{U}^\nu$ to one which is invariant under $\mathcal{S}_N$ and then diagonalizing H in this induced space $\mathfrak{U}^{\nu\uparrow}$. Given the basis (2.1) for $\mathfrak{U}^\nu$ it follows that the induced space $\mathfrak{U}^{\nu\uparrow}$ is spanned by the set

$$\{e^{\alpha}_{(\sigma\beta^0 s^0)(\rho\alpha^0 r^0)}\,|K^0;\,\alpha^0 r^0\rangle\ ;K^0,\,\alpha,\,\sigma\beta^0 s^0,\,\rho\ \text{ranging}\} . \tag{2.8}$$

Choosing the basis of $\mathfrak{U}^{\nu\uparrow}$ from (2.8) block-diagonalizes the matrix representation of H. A given block labeled by $\alpha(\sigma\beta^0 s^0)$ is square($f^{\alpha^0\uparrow\alpha}$ by $f^{\alpha^0\uparrow\alpha}$) and has elements which are independent of $\sigma\beta^0 s^0$. When the basis kets (2.1) for $\mathfrak{U}^\nu$ do not involve permutations of electrons between different centers, Hamiltonian matrix elements over these basis kets for $\mathfrak{U}^\nu$ need not involve four-, three-, or two-center exchange integrals; whereas, the matrix elements of H over the induced basis kets (2.8), in general, require these molecular integrals. In Sec. III we describe an alternative to this usual Rayleigh-Ritz variational approach in the induced space.

III. NEW VARIATIONAL SCHEME

The kets in the vector space $\mathfrak{U}^\nu$, in general, have components of those symmetries of $\mathcal{S}_N$ contained in the representation of $\mathcal{S}_N$ induced from the α^0th IR of $\mathcal{S}^0$. Here we will minimize the energy of a linear combination of kets in $\mathfrak{U}^\nu$ subject to the constraint that it has predetermined weights for all possible symmetry components arising from the zero-order symmetry $\alpha^0 r^0$. After the computation, approximate eigenkets for the individual symmetry components are obtained from the resulting constrained multistate ket by projection with the appropriate sequence-adapted matric basis elements. We find it notationally convenient here to suppress the symmetry labels $\alpha^0 r^0$, which apply to all the kets in the space $\mathfrak{U}^\nu$, thus obtaining abbreviations

$$|K^0\rangle = |K^0;\,\alpha^0 r^0\rangle , \tag{3.1}$$

$$e^{\alpha}_{\rho\sigma} = e^{\alpha}_{(\rho\alpha^0 r^0)(\sigma\alpha^0 r^0)} . \tag{3.2}$$

We stabilize, with respect to first-order variations in $\mathfrak{U}^\nu$ the expectation value $\langle\psi|H|\psi\rangle$, subject to the constraints

$$\langle\psi|e^{\alpha}_{\rho\sigma}|\psi\rangle = \delta_{\rho\sigma}a_\alpha . \tag{3.3}$$

Here, α, ρ, and σ range over all values for which the IR is contained in the representation induced from α^0 of $\mathcal{S}^0$; the ket $|\psi\rangle$ is contained in the vector space $\mathfrak{U}^\nu$; and the a_α are predetermined real constants. For a given α (with $a_\alpha \neq 0$) the multistate ket $|\psi\rangle$ has $f^{\alpha^0\uparrow\alpha}$ different orthogonal components $e^{\alpha}_{\rho\rho}|\psi\rangle$, among which there is no degeneracy. If the IR of $\mathcal{S}_N$ are chosen to be real and orthogonal, then we have

$$(e^{\alpha}_{\rho\sigma})^{\dagger} = e^{\alpha}_{\sigma\rho} . \tag{3.4}$$

Thus we have $\langle\psi|e^{\alpha}_{\rho\sigma}|\psi\rangle = \langle\psi|e^{\alpha}_{\sigma\rho}|\psi\rangle$, and not all the constraints in (3.3) are independent. The maximum number of linearly independent constraints is

$$\tfrac{1}{2}\textstyle\sum_\alpha f^{\alpha^0\uparrow\alpha}(f^{\alpha^0\uparrow\alpha}+1). \tag{3.5}$$

This number is reduced if some of the a_α are chosen to be zero, since $\langle\psi|e^{\alpha}_{\rho\rho}|\psi\rangle = 0$ implies $\langle\psi|e^{\alpha}_{\rho\sigma}|\psi\rangle = 0$. To satisfy all the constraints (3.3) the dimension of $\mathfrak{U}^\nu$ must, barring "accidental degeneracies," at least be equal to (3.5). To obtain good results a dimension somewhat greater would be preferable. Whatever choice for the a_α is made, the basis for $\mathfrak{U}^\nu$ must be flexible enough to satisfy the restrictions (3.3).

A choice for the a_α which may be employed with a computationally advantageous basis for $\mathfrak{U}^\nu$ is now briefly indicated. Choosing the separated atom solution to our stabilization problem to become a simple product ket $|K^0\rangle$ as in (2.5), gives

$$a_\alpha = \lim_{\vec{R}\to\infty}\langle\psi|e^{\alpha}_{\rho\rho}|\psi\rangle = \lim_{\vec{R}\to\infty}\langle K^0|e^{\alpha}_{\rho\rho}|K^0\rangle , \tag{3.6}$$

where $\vec{R}$ is a vector of interatomic distances, and $\vec{R}\to\infty$ means that every component of $\vec{R}$ becomes very large. Such a choice for the a_α (which do not vary with $\vec{R}$) could yield a reasonable choice for the a_α at finite $\vec{R}$. Equation (3.6) may be explicitly evaluated by retaining only the permutations of $e^{\alpha}_{\rho\rho}$ which do not interchange electrons between different atoms; that is, we retain only the permutations of $e^{\alpha}_{\rho\rho}$ which are in $\mathcal{S}^0$. This is conveniently accomplished by making a double-coset expansion[8] of $e^{\alpha}_{\rho\rho}$ and retaining only the identity double-coset term, to obtain

$$a_\alpha = \frac{f^\alpha g^0}{N!\,f^{\alpha^0}} . \tag{3.7}$$

Here f^α and f^{α^0} are the dimensions of α and α^0, and g^0 is the order of $\mathcal{S}^0$.

We next introduce Lagrange multipliers $\mathcal{E}_{\alpha\rho\sigma} = \mathcal{E}_{\alpha\sigma\rho}$ which are determined by the constraints (3.3) and by

$$\delta(\langle\psi|H|\psi\rangle - \sum_{\alpha\rho\sigma}\mathcal{E}_{\alpha\rho\sigma}\langle\psi|e^{\alpha}_{\rho\sigma}|\psi\rangle) = 0 . \tag{3.8}$$

Following well-known procedures[9,10] we obtain the eigenvalue equation

$$([H]^\nu - \sum_{\alpha\rho\sigma}\mathcal{E}_{\alpha\rho\sigma}[e^{\alpha}_{\rho\sigma}]^\nu)|\psi\rangle = 0 , \tag{3.9}$$

where $[H]^\nu$ and $[e^{\alpha}_{\rho\sigma}]^\nu$ are the representations of H and $e^{\alpha}_{\rho\sigma}$ on a basis for $\mathfrak{U}^\nu$. To solve (3.9) subject to the constraints (3. 3), a perturbation-expansion technique[10] coupled[11] with a Newton-Raphson iteration may be employed (see Appendix A).

To elucidate the physical interpretation of the Lagrange multipliers, we first note that the sequence-adapted matric basis elements $e^{\alpha}_{\rho\sigma}$ are nonunique[3] up to a unitary transformation $[U]^{\alpha}$:

$$e^{\alpha}_{\hat\rho\hat\sigma}=\sum_{\rho\sigma}[U]^{\alpha}_{\hat\rho\rho}\,e^{\alpha}_{\rho\sigma}[U^{-1}]^{\alpha}_{\sigma\hat\sigma}\ . \tag{3.10}$$

Now writing

$$\begin{aligned}\langle\psi|e^{\alpha}_{\hat\rho\hat\sigma}|\psi\rangle&=\sum_{\rho\sigma}[U]^{\alpha}_{\hat\rho\rho}\langle\psi|e^{\alpha}_{\rho\sigma}|\psi\rangle\,[U^{-1}]^{\alpha}_{\sigma\hat\sigma}\\&=a_{\alpha}\sum_{\rho\sigma}[U]^{\alpha}_{\hat\rho\rho}\,\delta_{\rho\sigma}[U^{-1}]^{\alpha}_{\sigma\hat\sigma}\\&=a_{\alpha}\delta_{\hat\rho\hat\sigma}\ ,\end{aligned}\tag{3.11}$$

we see that the constraints (3. 3) and $|\psi\rangle$ are not affected by this unitary transformation. Thus choosing $[U]^{\alpha}$ to be a unitary transformation which diagonalizes the Lagrange multiplier matrix with $\rho\sigma$th element $\mathcal{E}_{\alpha\rho\sigma}$, we have

$$\begin{aligned}\sum_{\rho\sigma}\mathcal{E}_{\alpha\rho\sigma}\,e^{\alpha}_{\rho\sigma}&=\sum_{\hat\rho\hat\sigma}\sum_{\rho\sigma}[U]^{\alpha}_{\hat\rho\rho}\mathcal{E}_{\alpha\rho\sigma}[U^{-1}]^{\alpha}_{\sigma\hat\sigma}\,e^{\alpha}_{\hat\rho\hat\sigma}\\&=\textstyle\sum_{\hat\rho}\mathcal{E}_{\alpha\hat\rho}\,e^{\alpha}_{\hat\rho\hat\rho}\ ,\end{aligned}\tag{3.12}$$

where $\mathcal{E}_{\alpha\hat\rho}$ is an eigenvalue of this Lagrange-multiplier matrix. These *stabilized* Lagrange multipliers $\mathcal{E}_{\alpha\hat\rho}$, and the corresponding sequence-adapted matric basis elements $e^{\alpha}_{\hat\rho\hat\rho}$, are independent of our initial choice of the sequence-adapted matric basis, though they are not independent of our choice for $\mathcal{U}^{\nu}$. Next, writing (3. 9) in terms of the stabilized matric basis and Lagrange multipliers, we have

$$\Big([H]^{\nu}-\sum_{\alpha\hat\rho}\mathcal{E}_{\alpha\hat\rho}\,[e^{\alpha}_{\hat\rho\hat\rho}]^{\nu}\Big)|\psi\rangle=0\ . \tag{3.13}$$

This we note is very similar to the generalized[4] Hirschfelder-Silbey equation which has been used for a starting point in perturbation expansions; Eq. (3. 13), however, is expressed on a general (finite or complete) vector space $\mathcal{U}^{\nu}$. If $\mathcal{U}^{\nu}$ is invariant under the $e^{\alpha}_{\rho\sigma}$, then we have

$$[e^{\alpha}_{\hat\sigma\hat\sigma}]^{\nu}\,[e^{\alpha}_{\hat\rho\hat\rho}]^{\nu}=\delta_{\hat\rho\hat\sigma}\,[e^{\alpha}_{\hat\rho\hat\rho}]^{\nu}\ , \tag{3.14}$$

and applying $[e^{\alpha}_{\hat\sigma\hat\sigma}]^{\nu}$ on the left to (3. 13), we obtain the usual Schrödinger equation

$$([H]^{\nu}-\mathcal{E}_{\alpha\hat\rho})\,[e^{\alpha}_{\hat\rho\hat\rho}]^{\nu}|\psi\rangle=0\ . \tag{3.15}$$

Thus if $\mathcal{U}^{\nu}$ is invariant under the $e^{\alpha}_{\rho\sigma}$, then the $\mathcal{E}_{\alpha\hat\rho}$ and $[e^{\alpha}_{\hat\rho\hat\rho}]^{\nu}|\psi\rangle$ are the single-state eigenvalues and eigenkets obtained when applying the usual Rayleigh-Ritz variational principle on the induced space $\mathcal{U}^{\nu\prime}$. When $\mathcal{U}^{\nu}$ is not invariant under the $e^{\alpha}_{\rho\sigma}$ [as is the case for a finite product basis of the form (2. 5)], Eq. (3. 15) may not hold; although, as the basis for $\mathcal{U}^{\nu}$ becomes more and more nearly complete, $\mathcal{E}_{\alpha\hat\rho}$ and $[e^{\alpha}_{\hat\rho\hat\rho}]^{\nu}|\psi\rangle$ are expected to converge to the exact single-state eigenvalue and eigenket. Thus the Lagrange multiplier $\mathcal{E}_{\alpha\hat\rho}$ and projected ket $[e^{\alpha}_{\hat\rho\hat\rho}]^{\nu}|\psi\rangle$ are our νth approximation to the $\rho\alpha$th eigenvalue and eigenket of the complete spin-free Hamiltonian H.

IV. DISCUSSION

The multistate variational calculation yields a multistate ket accurate to a degree limited by the size and suitability of the basis. Since we may choose a product basis as in (2. 5) with A, B, C, ... referring to different atoms, we may avoid four-, three-, and two-center exchange integrals in a polyatomic calculation. Near the separated atom limit, such a limited product basis is expected to yield a good approximation to the exact multistate ket, if the a_{α} weighting factors are chosen as in (3. 7). The computed multistate ket then yields projected approximations to a number of states possibly including some which are not observed, i. e., states forbidden by the spin-free[1] Pauli exclusion principle. Indeed, as the number of centers increases, the number of states increases as does the number of constraints, so that practical computations become discouraged; for example, with six hydrogen atoms we have 76 states and 398 constraints, while for one triplet oxygen atom and two hydrogen atoms we have 10 states and 13 constraints.

The sequence-adapted IR matrix elements, which appear in the definition (2. 6) of the $e^{\alpha}_{\rho\sigma}$, may be computed when $f^{\alpha^0,\alpha}=1$ by a number of different methods discussed elsewhere.[3,5,12] When we have $f^{\alpha^0,\alpha}\geq 2$, the same methods may be applied[3] if a chain of groups intermediate between $\mathcal{S}^0$ and S_N may be found such that the pertinent intermediate frequencies are no greater than 1. In addition, we note that the Pauling numbers[13] for generalized structure projectors[5] are proportional to the desired $[P]^{\alpha}_{\rho\sigma}$.

The Hilbert space of symmetry $\alpha^0\gamma^0$ is a complete space in which to expand the multistate ket. However, in a limited configuration-interaction treatment it may be desired to allow kets of another local permutational symmetry $\alpha'^0\gamma'^0$ to mix in. Alternatively, it may be desired to obtain approximations to additional states. The method for accomplishing these ends is briefly outlined in Appendix B. In Appendix C another generalization is described which takes into account point-group symmetry operations which transfer electrons from one atom to another. The variational scheme described here could be revised or generalized in several other ways too; for example, one could neglect the constraints of (3. 3) for $\rho\neq\sigma$ or replace $\mathcal{S}^0$ and S_N both by different groups involving point-group symmetry. However, the versions described here are thought to hold the most promise in treating intermolecular exchange energies.

The variational scheme proposed here appears computationally feasible at least for small molecules. It differs from the usual Rayleigh-Ritz variational procedure in considering simultaneously all the states which arise from a given separated-atom limit and a given local-permutational symmetry. The multistate variational scheme formally applies when A, B, C, ... refer, not only to atoms, but also to shells in an atom or molecule, or molecules in a polymolecular complex. Finally we note that perturbation SCF or other developments based on such a multistate variational principle are possible.

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APPENDIX A

Here we indicate an iterative procedure to solve (3.9) subject to the constraints (3.3). First following Byers Brown[10] we replace the $\mathcal{E}_{\alpha\rho\sigma}$ by variables $\epsilon_{\alpha\rho\sigma}$ and consider the (fictitious) Hamiltonian

$$\mathcal{H}^{\nu}(\vec{\epsilon}) = [H]^{\nu} - \sum_{\alpha\rho\sigma} \epsilon_{\alpha\rho\sigma} [e^{\alpha}_{\rho\sigma}]^{\nu} , \tag{A1}$$

where $\vec{\epsilon}$ is the vector collection of the $\epsilon_{\alpha\rho\sigma}$. We let $|\vec{\epsilon}\rangle$ and $E(\vec{\epsilon})$ denote the eigenket and eigenvalue which correspond to the desired separated-atom limit

$$\mathcal{H}^{\nu}(\vec{\epsilon})|\vec{\epsilon}\rangle = E(\vec{\epsilon})|\vec{\epsilon}\rangle . \tag{A2}$$

Using the Hellman-Feyman theorem we obtain

$$\frac{\partial E(\vec{\epsilon})}{\partial \epsilon_{\alpha\rho\sigma}} = -\frac{\langle \vec{\epsilon} | e^{\alpha}_{\rho\sigma} | \vec{\epsilon} \rangle}{\langle \vec{\epsilon} | \vec{\epsilon} \rangle} . \tag{A3}$$

Assuming

$$\langle \vec{\epsilon} | \vec{\epsilon} \rangle = \sum_{\alpha\rho} a_{\alpha} = 1 , \tag{A4}$$

it is seen that the constraint conditions (3.3) will be satisfied when

$$\frac{\partial E(\vec{\epsilon})}{\partial \epsilon_{\alpha\rho\sigma}} = -\delta_{\rho\sigma} a_{\alpha} . \tag{A5}$$

Next, following Byers Brown[10] and Chong[11] we expand $E(\vec{\epsilon})$ in a multiple perturbation series about, say, $\vec{\epsilon} = \vec{\epsilon}_i$ and then take derivatives to obtain

$$\frac{\partial E(\vec{\epsilon})}{\partial \epsilon_{\alpha\rho\sigma}} = E^{(1)}_{\alpha\rho\sigma}(\vec{\epsilon}_i) + \sum_{\beta\tau\omega} \{E^{(2)}_{\alpha\rho\sigma,\beta\tau\omega}(\vec{\epsilon}_i) + E^{(2)}_{\beta\tau\omega,\alpha\rho\sigma}(\vec{\epsilon}_i)\} \times (\epsilon_{\beta\tau\omega} - \epsilon_{\beta\tau\omega;\,i}) + \cdots . \tag{A6}$$

Here the first- and second-order perturbation energies are, as usual,

$$E^{(1)}_{\alpha\rho\sigma}(\vec{\epsilon}_i) = -\langle \vec{\epsilon}_i | e^{\alpha}_{\rho\sigma} | \vec{\epsilon}_i \rangle , \tag{A7}$$

$$E^{(2)}_{\alpha\rho\sigma,\beta\tau\omega}(\vec{\epsilon}_i) = \langle \vec{\epsilon}_i | e^{\alpha}_{\rho\sigma} [E(\vec{\epsilon}_i) - \mathcal{H}^{\nu}(\vec{\epsilon}_i)]^{-1} e^{\beta}_{\tau\omega} | \vec{\epsilon}_i \rangle , \tag{A8}$$

where the resolvent operator in (A8) yields zero when applied to $|\vec{\epsilon}_i\rangle$. The first-order energies (A7) form a vector, denoted $\vec{\mathrm{E}}^{(1)}_i$, and the second-order energies (A8) form a square matrix, denoted $\overleftrightarrow{\mathrm{E}}^{(2)}_i$.

Now as suggested by Chong,[11] we apply the Newton-Raphson method.[9] The $(i+1)$th iterate $\vec{\epsilon}_{i+1}$ is obtained from the ith iterate $\vec{\epsilon}_i$ by setting the right-hand side of (A5) equal to the right-hand side of (A6) truncated at second-order energies,

$$\vec{\epsilon}_{i+1} - \vec{\epsilon}_i = (\overleftrightarrow{\mathrm{E}}^{(2)}_i)^{-1} \cdot (-\vec{\mathrm{E}}^{(1)}_i - \vec{\mathrm{a}}) , \tag{A9}$$

where $\vec{\mathrm{a}}$ is the vector collection of the $a_{\alpha}\delta_{\rho\sigma}$. Once this, or some other method converges, the Lagrange multipliers $\mathcal{E}_{\alpha\rho\sigma}$ are given:

$$\mathcal{E}_{\alpha\rho\sigma} = \epsilon_{\alpha\rho\sigma} + E(\vec{\epsilon}) . \tag{A10}$$

Which root of $\mathcal{H}^{\nu}(\vec{\epsilon})$ correlates with the desired separated atom limit and a "good" initial guess for an iteration procedure might be obtained by considering the $\vec{\mathcal{E}}$ from previous calculations at nearby interatomic separations. Thus we might begin near the separated-atom limit, where good initial guesses are available, and work in to smaller interatomic separations.

APPENDIX B

Here the multistate variational scheme is extended to include two different local-permutational symmetries $\alpha^0\gamma^0$ and $\alpha'^0\gamma'^0$. We let $\mathcal{U}^{\nu}$ denote a space of kets of both local symmetries and minimize $\langle \psi | H | \psi \rangle$ with $|\psi\rangle \in \mathcal{U}^{\nu}$ subject to the constraints

$$\langle \psi | e^{\alpha}_{\rho\sigma} | \psi \rangle = a_{\alpha}\delta_{\rho\sigma} , \tag{B1}$$

$$\langle \psi | e^{\alpha}_{\rho\sigma'} | \psi \rangle = \langle \psi | e^{\alpha}_{\rho'\sigma} | \psi \rangle = 0 , \tag{B2}$$

$$\langle \psi | e^{\alpha}_{\rho'\sigma'} | \psi \rangle = a'_{\alpha}\delta_{\rho'\sigma'} . \tag{B3}$$

Here ρ and σ are abbreviations for $(\rho\alpha^0\gamma^0)$ and $(\sigma\alpha^0\gamma^0)$ as before, while ρ' and σ' are abbreviations for $(\rho'\alpha'^0\gamma'^0)$ and $(\sigma'\alpha'^0\gamma'^0)$. We note that if either $\langle \psi | e^{\alpha}_{\rho\rho} | \psi \rangle = 0$ or $\langle \psi | e^{\alpha}_{\sigma'\sigma'} | \psi \rangle = 0$, then the relation $\langle \psi | e^{\alpha}_{\rho\sigma'} | \psi \rangle = 0$ is automatically satisfied and is not an independent constraint. The development of the equations is very similar to the previous case in Sec. III. The unitary transformation which diagonalizes the matrix of Lagrange multipliers can in the present case mix local-permutational symmetries, however. This type of treatment could be extended to an even greater number of local-permutational symmetries; in the limit the multistate ket would contain approximations to $N!$ states.

APPENDIX C

In general, more states than counted by inducing α^0 of S^0 into S_N will arise from a given separated-atom limit. Including a consideration of the point-group symmetry will encompass all (barring accidental degeneracy) these states. Part of the problem may be treated by traditional *descent-in-symmetry* methods; we choose the kets of $\mathcal{U}^{\nu}$ to be symmetry-adapted to the intersection $\mathcal{G}_{pg} \cap \mathcal{G}^0_{pg}$ of the molecular point group $\mathcal{G}_{pg}$ and the outer product $\mathcal{G}^0_{pg}$ of isolated atom point groups. The basis kets of $\mathcal{U}^{\nu}$ may still be expressed as product kets as in (2.5), and we account for the symmetry reduction in going from $\mathcal{G}^0_{pg}$ to $\mathcal{G}_{pg} \cap \mathcal{G}^0_{pg}$. The remaining molecular point-group symmetry will be discussed using the factor group

$$\mathcal{F}_{pg} = \mathcal{G}_{pg} / (\mathcal{G}_{pg} \cap \mathcal{G}^0_{pg}) \ . \tag{C1}$$

This factor group may also be described as the subgroup of $\mathcal{G}_{pg}$ which "permutes" identical nuclei among themselves. For nonplanar molecules, $\mathcal{F}_{pg}$ is simply $\mathcal{G}_{pg}$; for nonlinear planar molecules, $\mathcal{F}_{pg}$ is the subgroup of $\mathcal{G}_{pg}$ which does not involve reflection in the molecular plane; and for linear molecules it is either the identity group or the inversion group.

Much of the same formalism of this paper now holds if in place of $\mathcal{S}_N$ we refer to the product group $\mathcal{S}_N \mathcal{F}_{pg}$. The sequence-adapted matric basis elements as in (2.6) are taken to be for the sequence $\mathcal{S}^0 \subseteq \mathcal{S}_N \mathcal{F}_{pg}$, and the material of Sec. II remains unchanged. In Sec. III, Eq. (3.4) is replaced by $(e^{\alpha}_{\rho\sigma})^{\dagger} = e^{\bar{\alpha}}_{\bar{\sigma}\bar{\rho}}$, where $\bar{\alpha}$ denotes the IR complex conjugate to α, and (3.6) may yield a result different from that in (3.7); however, the rest of the formalism is similar.

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