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New methods which avoid the repeated constructions of aggregate Hamiltonian matrices over antisymmetric basis states generally required in conventional calculations of adiabatic potential energy surfaces are reported for ab initio studies of the structures, spectra, and chemical reactions of molecules and other forms of matter. A representational basis in the form of an outer spectral product of atomic eigenstates, employed in the absence of overall electron antisymmetry, is shown to facilitate development of an exact atomic-pair expression for aggregate Hamiltonian matrices. Unphysical (no-Pauli) eigenstates spanned by the atomic product basis are identified and eliminated by a unitary transformation of the Hamiltonian matrix obtained from the matrix representative of the aggregate electron antisymmetrizer. Hermitian atomic and atomic-pair interaction matrices are defined which individually have appropriate asymptotic separation limits and can be constructed once and for all employing unitary transformations of antisymmetric adiabatic diatomic eigenstates and associated potential energy curves. The aggregate Hamiltonian matrix constructed in this way includes the effects of overall electron antisymmetry and incorporates Wigner rotation matrices for representation of all angular dependencies. A particular implementation of the theory which explicitly enforces the limit of closure in spectral-product calculations is seen to correspond to adoption of canonically orthogonalized linearly-independent antisymmetrized diatomic states obtained from conventional computational procedures.

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# Atomic Spectral Methods for Molecular Electronic Structure Calculations: Atomic-Pair Representations of Aggregate Hamiltonian Matrices†

## - PREPRINT -

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# Abstract

New methods which avoid the repeated constructions of aggregate Hamiltonian matrices over antisymmetric basis states generally required in conventional calculations of adiabatic potential energy surfaces are reported for *ab initio* studies of the structures, spectra, and chemical reactions of molecules and other forms of matter. A representational basis in the form of an outer spectral product of atomic eigenstates, employed in the absence of overall electron antisymmetry, is shown to facilitate development of an exact atomic-pair expression for aggregate Hamiltonian matrices. Unphysical (non-Pauli) eigenstates spanned by the atomic product basis are identified and eliminated by a unitary transformation of the Hamiltonian matrix obtained from the matrix representative of the aggregate electron antisymmetrizer. Hermitian atomic and atomic-pair interaction matrices are defined which individually have appropriate asymptotic separation limits and can be constructed once and for all employing unitary transformations of antisymmetric adiabatic diatomic eigenstates and associated potential energy curves. The aggregate Hamiltonian matrix constructed in this way includes the effects of overall electron antisymmetry and incorporates Wigner rotation matrices for representation of all angular dependencies. A particular implementation of the theory which explicitly enforces the limit of closure in spectral-product calculations is seen to correspond to adoption of canonically orthogonalized lineraly-independent antisymmetrized diatomic states obtained from conventional computational procedures. Illustrative applications to the well-known low-lying doublet and quartet states of the $H_3$ molecule demonstrate that the eigensurfaces of the antisymmetrizer can anticipate the structures of the more familiar potential energy surfaces, which are found to be in satisfactory accord with values obtained employing prior aggregate antisymmetrization. Analyses of previously devised atoms-in-molecules and diatomic-in-molecules methods emphasize the importance of aggregate basis-state orthogonality, use of strictly Hermitian matrix representatives, and unitary transformations of atomic and diatomic fragment information in such connections, attributes which have generally not been included in applications of these otherwise promising approaches. The present development is seen to circumvent the limitations of these early semi-empirical methods, providing a convergent *ab initio* formalism suitable for computational applications.

## 1.0 Introduction

Theoretical studies of the structures, electromagnetic spectra, and chemical reactions of molecules and other forms of matter require accurate approximations to the complex (Born-Oppenheimer) potential energy surfaces describing their ground and excited electronic states [1]. Such surfaces would preferably be available in forms that allow for convenient solution of the associated molecular Schrödinger equation, and would also provide for study of the avoided crossings and surface intersections that can give rise to non-adiabatic dynamical behaviors [2]. The ability to perform simultaneous quasi-classical molecular dynamics (MD) and electronic structure calculations, in which the electronic surfaces are determined in the course of MD simulation at the particular aggregate configurations sampled [3], would be highly desireable in cases involving sufficiently heavy atoms, provided that the electronic surfaces employed can include the subtleties associated with the possible presence of large numbers of interacting aggregate electron configurations [4].

Computational methods currently employed for the aforementioned purposes commonly entail repeated calculations of large numbers of one-and two-electron integrals over explicitly antisymmetrized basis states in construction of a many-electron Hamiltonian matrix for a range of atomic spatial arrangements, followed by determination of the energies and associated eigenfunctions of selected electronic states at each atomic arrangement and construction of expectation values corresponding to physical properties of interest. Considerable progress has been made in implementing and applying this general approach in *ab initio* calculations [5,6], as well as in the widely employed density-funtional approximation [7]. Nevertheless, it would be highly desireable to devise new methods which can avoid the repeated calculations required in the conventional approaches, can circumvent determinations of total molecular energies and their associated differencing problems in favor of calculations of constituent atomic energies and atomic-pair interaction energies, and can be applied to both ground and electronically-excited states on a common basis.

In the present report, an atomic-pair-interaction approach to *ab-initio* studies of molecules and other aggregates is described based on a previously described atomic spectral-product representation of the electronic degrees of freedom [8-12]. The development accommodates the incorporation of *ab-initio* diatomic information in a rigorous fashion free of the subjective *ad hoc* assumptions and approximations which have rendered such fragment-based approaches largely semi-empirical in nature [13,14]. The present method is ultimately based on conventional variational calculations in $L^2$ representations of many-electron states, guaranteeing its bounded (Hylleraas-Undheim) convergence when closure is achieved, in which limit the distinction between use of atomic-product and explicitly antisymmetrized aggregate basis states is shown to become inconsequential. As presented here, the theory is applicable to finite atomic aggregates which dissociate into neutral species on their lowest-lying potential energy surfaces, but which can involve arbitrary admixtures of covalent, ionic, van der Waals, and metallic interatomic interactions. Applications of the approach to ionic systems, or to neutral systems which can give rise to ion-pair states in asymptotic separation limits, require only minor, largely self-evident, modifications of the present development.

The atomic spectral-product basis employed in the development is known to span the totally antisymmetric irreducible representation of the aggregate electron symmetric group once and only once, making it suitable for analytical and computational studies of the electronic structures of molecules and other forms of matter [8-12]. The matrix representative of the aggregate electron antisymmetrizer constructed in the spectral-product basis can be employed in separating the totally antisymmetric and non-totally-antisymmetric (non-Pauli) states spanned by the basis, and in correspondingly isolating the physically significant block of the Hamiltonian matrix by unitary transformation. Hermitian matrix representations of atomic and atomic-pair operators are devised in this way which *individually* have well-defined asymptotic separation limits, and which need be constructed only once for multiple applications. These attributes of the approach facilitate development of an *ab initio* unitary transformation formalism which provides an exact atomic-pair representation of aggregate Hamiltonian matrices, including particularly modifications due to aggregate electron antisymmetry of the bare atomic-pair interactions consequent of their incorporation in the atomic aggregate. The development furthermore allows for the incorporation of Wigner rotation matrices in an efficient representation of all angular dependences of the interaction matrix elements [15].

A particular computational implementation of the theoretical development is described which enforces closure limits over the formally infinite spectral sums required to achieve wave function antisymmetry, providing expressions which can be evaluated with largely standard *ab-initio* computational methods [5-7]. Illustrative applications in the case of the low-lying doublet and quartet states of the $H_3$ molecule demonstrate that the eigensurfaces of the electron antisymmetrizer can anticipate the structures of the corresponding more familiar potential energy surfaces, which are found to be in accord with values obtained employing conventional computational methods. This particular implementation of the theory also helps to identify the origins of complications encountered in applications of related semi-empirical atoms-in-molecules [13] and diatomic-in-molecules [14] formalism based on explicitly antisymmetric aggregate basis states, which issues have apparently precluded their widespread adoption to date as viable computational approaches. Modifications of these approaches based on the present analysis are seen to lead to potentially convergent *ab initio* computational formalisms

The theory is described in Section 2, where the atomic spectral representation of aggregate electronic degrees of freedom is defined, the unitary transformation formalism for isolation of the physical portion of the spectrum and for incorporation of *ab initio* diatomic information is described, and the exact atomic-pair form of the aggregate Hamiltonian matrix reported. The particular computational implementation of the approach devised is described and illustrative calculations of the doublet and quartet potential energy surfaces of $H_3$ provided in Section 3. Comparative and concluding remarks made in Section 4 place the present development in the context of the aforementioned earlier semi-empirical approaches [13,14], help to clarify the origins of complications encountered in their applications, and demonstrate how the present development circumvents these difficulties.

## 2.0 Theory

The atomic spectral-product approach to aggregate electronic structure is described in Section 2.1, the unitary transformation formalism for incorporation of diatomic information is presented in Section 2.2, and the resulting exact atomic-pair form of the aggregate Hamiltonian matrix is reported in Section 2.3.

### 2.1 Atomic Spectral-Product Formalism

Solutions of the Schrödinger equation [16]

$$\hat{H}(\boldsymbol{r}:\boldsymbol{R})\boldsymbol{\Psi}(\boldsymbol{r}:\boldsymbol{R}) = \boldsymbol{\Psi}(\boldsymbol{r}:\boldsymbol{R})\cdot\mathbf{E}(\boldsymbol{R}) \tag{1}$$

for an $N$-atom molecule or other finite atomic aggregate with Hamiltonian operator

$$\hat{H}(\boldsymbol{r}:\boldsymbol{R}) = \sum_{\alpha=1}^{N}\Big\{\hat{H}^{(\alpha)}(\boldsymbol{i}) + \sum_{\beta=\alpha+1}^{N}\hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})\Big\} \tag{2}$$

can be constructed employing a formally complete orthonormal square-integrable ($L^2$) outer-spectral-product representation of the form [8-12]

$$\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) = \Big\{\boldsymbol{\Phi}^{(1)}(\boldsymbol{1})\otimes\boldsymbol{\Phi}^{(2)}(\boldsymbol{2})\otimes\cdots\boldsymbol{\Phi}^{(N)}(\boldsymbol{n})\Big\}_{O}. \tag{3}$$

The Hamiltonian operator $\hat{H}(\boldsymbol{r}:\boldsymbol{R})$ in Eqs. (1) and (2) includes a sum over atomic terms

$$\hat{H}^{(\alpha)}(\boldsymbol{i}) = \sum_{i}^{n_\alpha}\Big\{-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{i'=i+1}^{n_\alpha}\frac{e^2}{r_{ii'}}\Big\} \tag{4}$$

and a sum over pairwise-atomic Coulombic interaction terms [17]

$$\hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) = \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - \sum_{i}^{n_\alpha}\frac{Z_\beta e^2}{r_{i\beta}} - \sum_{j}^{n_\beta}\frac{Z_\alpha e^2}{r_{j\alpha}} + \sum_{i}^{n_\alpha}\sum_{j}^{n_\beta}\frac{e^2}{r_{ij}}, \tag{5}$$

where $\boldsymbol{r}$ and $\boldsymbol{R}$ refer to all $n_t$ aggregate electron and $N$ atomic-position coordinates, respectively. The desired row vector of eigenfunctions $\boldsymbol{\Psi}(\boldsymbol{r}:\boldsymbol{R})$ and the diagonal matrix of associated eigenvalues $\mathbf{E}(\boldsymbol{R})$ of Eq. (1) generally include both physically significant and unphysical (non-Pauli) solutions [12]. The row vectors $\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i})$ in Eq. (3) comprise the orthonormal antisymmetric multiplet eigenstates of the constituent atoms ($\alpha = 1$ to $N$) specified by the quantum numbers $(E, L, M_L, S, M_S, P)_\alpha$ [18], with $\boldsymbol{i}$ ($\boldsymbol{j}$) referring to the coordinates relative to the atomic center $\boldsymbol{R}_\alpha$ ($\boldsymbol{R}_\beta$) of the $n_\alpha$ ($n_\beta$) electrons arbitrarily assigned to the atom $\alpha$ ($\beta$). The atomic eigenstates can be variationally determined in $L^2$ basis-state representations and need not be exact eigenfunctions of the corresponding atomic Hamiltonian operators for the ensuing development to converge, so long as the denumerably infinite outer-product ($\otimes$) Hilbert space of Eq. (3) includes a suitable closure limit over the range of atomic configurations $\boldsymbol{R}$ of interest [19]. The subscript "$O$" in Eq. (3) indicates the adoption of a particular ordering convention for the vector sequence of spectral-product functions employed, the consequences of which convention are indicated when appropriate in the sequel. More detailed descriptions of this and of the other notational conventions of Eqs. (1) to (5) are reported elsewhere [8-12].

Employing the formally complete orthonormal basis of Eq. (3) in variational solution of Eq. (1) gives the familiar matrix Schrödinger equation

$$\mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{H}}(\boldsymbol{R}) = \mathbf{U}_{\mathbf{H}}(\boldsymbol{R}) \cdot \mathbf{E}(\boldsymbol{R}), \tag{6}$$

where the columns of the unitary matrix $\mathbf{U}_{\mathbf{H}}(\boldsymbol{R})$ which diagonalizes the Hermitian Hamiltonian matrix $\mathbf{H}(\boldsymbol{R})$ provide the desired eigenvectors $\boldsymbol{\Psi}(\boldsymbol{r} : \boldsymbol{R}) = \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{H}}(\boldsymbol{R})$ following commonly employed labelling and ordering conventions [16]. The Hamiltonian matrix of Eq. (6),

$$\mathbf{H}(\boldsymbol{R}) \equiv \langle \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) | \hat{H}(\boldsymbol{r} : \boldsymbol{R}) | \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \rangle = \sum_{\alpha=1}^{N} \Big\{ \mathbf{H}^{(\alpha)} + \sum_{\beta=\alpha+1}^{N} \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \Big\}, \tag{7}$$

includes constant atomic terms $\mathbf{H}^{(\alpha)} \equiv \langle \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) | \hat{H}^{(\alpha)}(\boldsymbol{i}) | \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \rangle$ and atomic-pair interaction terms $\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \equiv \langle \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) | \hat{V}^{(\alpha,\beta)}(\boldsymbol{i}; \boldsymbol{j} : \boldsymbol{R}_{\alpha\beta}) | \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \rangle$ which are the Hermitian matrix representatives of the corresponding atomic [Eq. (4)] and interaction [Eq. (5)] operators in the aggregate Hamiltonian operator of Eq. (2). The atomic energy matrix $\mathbf{H}^{(\alpha)}$ includes only diagonal multiplet energies which are independent of atomic position, consequent of choosing the orthonormal atomic states $\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i})$ as eigenstates or pseudo-eigenstates of the respective atomic Hamiltonian operators, whereas the interaction matrix $\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ is generally non-diagonal and depends explicitly upon the vector separation $\boldsymbol{R}_{\alpha\beta}$ of the two indicated atoms, but not upon the individual laboratory-frame positions of the two atoms, nor upon the position vectors of the other $(N-2)$ atoms in the aggregate.

The particularly simple form of Eq. (7) is largely a consequence of the orthonormality of the spectral-product basis employed in the absence of prior enforcement of overall aggregate electron antisymmetry, the use of atomic multiplet eigenstates in the representation, and the atomic pairwise-additive nature of the interaction terms in the Hamiltonian operator of Eq. (2). It has been shown that the basis of Eq. (3) spans the totally antisymmetric representation of the aggregate $n_t$-electron permutation (or symmetric - $S_{n_t}$) group once and only once in the limit of closure, although other unphysical non-totally-antisymmetric (non-Pauli) representations of $S_{n_t}$ are also spanned by the basis [12,20-24].

The totally antisymmetric eigenstates and the non-Pauli eigenstates obtained from Eqs. (1) to (7) can be separated by constructing the transformed Hamiltonian matrix

$$\mathbf{H}_{\mathbf{S}}(\boldsymbol{R}) \equiv \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R}) = \sum_{\alpha=1}^{N} \Big\{ \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) + \sum_{\beta=\alpha+1}^{N} \mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) \Big\}$$

$$= \begin{pmatrix} \{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} & \{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{pu} \\ \{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{up} & \{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{uu} \end{pmatrix} \rightarrow \begin{pmatrix} \{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} & \mathbf{0} \\ \mathbf{0} & \{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{uu} \end{pmatrix}, \qquad (8)$$

where $\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) \equiv \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{H}^{(\alpha)} \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ and $\mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) \equiv \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ refer to transformations of the individual atomic and interaction matrices in Eq. (7), $\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{pp}$ and $\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{uu}$ are the physical (*pp*) and unphysical (*uu*) blocks of the transformed Hamiltonian matrix which provide the antisymmetric and the non-Pauli solutions, respectively, and the off-diagonal blocks vanish in the limit (→) of spectral closure [9-12].

The unitary transformation matrix $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ required to accomplish the partitioning of Eq. (8) is obtained from diagonalization

$$\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{S}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R}) = \mathbf{S}_d(\boldsymbol{R}) = \begin{pmatrix} \{\mathbf{S}_d(\boldsymbol{R})\}_{pp} & \mathbf{0} \\ \mathbf{0} & \{\mathbf{S}_d(\boldsymbol{R})\}_{uu} \end{pmatrix} \rightarrow \begin{pmatrix} Q\mathbf{I}_{pp} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \qquad (9)$$

of the Hermitian matrix representative of the antisymmetrizer $\hat{P}_A$ constructed in the spectral-product basis,

$$\mathbf{S}(\boldsymbol{R}) \equiv Q^{1/2} \langle \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) | \hat{P}_A | \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) \rangle = \langle \hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) | \hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) \rangle, \qquad (10)$$

which is seen to be proportional to the metric matrix of the explicitly antisymmetrized spectral-product basis. The normalization of the antisymmetrizer employed in the present development, $\hat{P}_A \equiv (n_t!)^{-1/2}(n_1!n_2!\cdots n_N!)^{-1/2}\sum_{p=1}^{n_t!}(-1)^{\delta_p}\hat{P}_p$, is chosen to insure that $\mathbf{S}(\boldsymbol{R} \rightarrow \infty) \rightarrow \mathbf{I}$ when all the atomic states of Eq. (3) from the different atoms no longer "overlap" in the sense of Eq. (10) in the complete dissociation limit. Adoption of this normalization convention, which is commonly employed to insure unity normalization of the antisymmetrized product basis $\hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R})$ in the limit $(\boldsymbol{R} \to \infty)$ [13], gives the value $Q = n_t!/(n_1!n_2! \cdots n_N!)$ for the redundancy factor of the antisymmetrized basis appearing in Eq. (10) [22].

The non-negative eigenvalue matrix $\mathbf{S}_d(\boldsymbol{R})$ in Eq. (9) is partitioned into an upper diagonal $\{\mathbf{S}_d(\boldsymbol{R})\}_{pp}$ containing the largest eigenvalues ordered in decreasing value, which tend to the indicated common redundancy factor $Q$ in the closure limit, and a lower diagonal $\{\mathbf{S}_d(\boldsymbol{R})\}_{uu}$ of eigenvalues which tend to zero in this limit [9-12]. The eigenvalues are so ordered by appropriate arrangement of the columns of the transformation matrix $\mathbf{U}_\mathbf{S}(\boldsymbol{R})$, whereas the dimensions of the blocks $\{\mathbf{H}_\mathbf{S}(\boldsymbol{R})\}_{pp/uu}$ of Eq. (8) in finite order are determined by that block of the diagonal matrix $\mathbf{S}_d(\boldsymbol{R})$ of Eq. (9) subjectively selected as its physical part in the particular atomic spectral-product representation employed.

The unitary transformation matrix $\mathbf{U}_\mathbf{S}(\boldsymbol{R})$ of Eq. (9) obtained from the metric matrix of Eq. (10) is responsible for incorporating the non-local effects of inter-atomic aggregate electron permutation symmetry in the Hamiltonian matrix of Eq. (7) by virture of Eq. (8) [9-12]. That is, the diagonalization of Eq. (9) corresponds to construction of eigenstates of the Hermitian antisymmetrizer in the spectral-product basis, so that the columns of the transformation matrix $\mathbf{U}_\mathbf{S}(\boldsymbol{R})$ provide the eigenstates of the operator $\hat{P}_A$ in the spectral-product representation in the form

$$\boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r} : \boldsymbol{R}) \equiv \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{U}_\mathbf{S}(\boldsymbol{R}) \to \big\{\{\boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r} : \boldsymbol{R})\}_p, \{\boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r} : \boldsymbol{R})\}_u\big\}. \tag{11}$$

Here, $\{\boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r} : \boldsymbol{R})\}_p$ contains the totally antisymmetric states corresponding to the non-zero eigenvalues of the antisymmetrizer and $\{\boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r} : \boldsymbol{R})\}_u$ contains the non-Pauli states corresponding to the zero eigenvalues of the antisymmetrizer in the closure limit. Consequently, it follows that Eq. (8) constitutes a unitary transformation of the Hamiltonian matrix of Eq. (7) constructed in the spectral-product basis to the orthonormal permutation-symmetry-adapted representation of Eq. (11).

Equations (9) to (11) indicate that the spectrum of $\hat{P}_A$ acting in the domain of the spectral-product basis of Eq. (3) is that of a compact Hermitian operator [25], with zero providing a lower limiting point of accumulation of the spectrum and the associated non-Pauli states $\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R})\}_u$ of Eq. (11) corrersponding to its null space $\hat{P}_A\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R})\}_u \to \mathbf{0}$, whereas the antisymmetric states $\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R})\}_p$ of Eq. (11) are associated with the upper limiting point, $\hat{P}_A\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R})\}_p \to Q^{1/2}\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R})\}_p$, and correspond to its non-vanishing point spectrum.

The condition $\mathbf{S}(\boldsymbol{R}\to\infty)\to\mathbf{I}$ indicated above can always be satisfied for a sufficiently large dissociation limit ($\boldsymbol{R}\to\infty$) which separates all atoms beyond the range of all atomic eigenstate overlap in any particular denumerable $L^2$ spectral-product representation. In this limit, the transformation matrix of Eq. (9) becomes a constant unitary matrix $\mathbf{U}_{\mathbf{S}}(\infty)$ [$\equiv \mathbf{U}_{\mathbf{S}}(\boldsymbol{R}\to\infty)$], the physical portion of Eq. (11) becomes a unitary transformation of the entire spectral-product basis of Eq. (3) [$\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R}\to\infty)\to\boldsymbol{\Phi}(\boldsymbol{r}:\infty)\cdot\mathbf{U}_{\mathbf{S}}(\infty)$], the unphysical portion of Eq. (11) is correspondingly null, the interaction matrices of Eq. (7) vanish [$\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}\to\infty)\to\mathbf{0}$], and the Hamiltonian matrix of Eq. (8) becomes

$$\mathbf{H}_{\mathbf{S}}(\boldsymbol{R}\to\infty)\to\mathbf{U}_{\mathbf{S}}(\infty)^{\dagger}\cdot\mathbf{H}(\boldsymbol{R}\to\infty)\cdot\mathbf{U}_{\mathbf{S}}(\infty)=\mathbf{U}_{\mathbf{S}}(\infty)^{\dagger}\cdot\Big\{\sum_{\alpha=1}^{N}\mathbf{H}^{(\alpha)}\Big\}\cdot\mathbf{U}_{\mathbf{S}}(\infty). \quad (12)$$

In view of the unitary nature of the transformation of Eq. (12), the aggregate energies in the dissociation limit are seen to be sums of the individual non-interacting atomic energies, as anticipated. Moreover, although the unitary matrix $\mathbf{U}_{\mathbf{S}}(\infty)$ obtained from Eq. (9) is formally arbitrary in this limit, as a consequence of the degeneracy of the eigenvalues of the metric matrix [$\mathbf{S}(\boldsymbol{R}\to\infty)\to\mathbf{I}$], it is possible to choose the aggregate eigenfunctions $\boldsymbol{\Phi}(\boldsymbol{r}:\infty)\cdot\mathbf{U}_{\mathbf{S}}(\infty)$ as states of good total aggregate spin multiplicity, and of other possible aggregate point-group symmetry, insuring that $\mathbf{U}_{\mathbf{S}}(\infty)$ commutes with the indicated atomic matrix sum in Eq. (12). In this case the Hamiltonian matrix of Eq. (12) is, of course, identical with the indicated sum of unperturbed atomic energies.

The absence of explicit inter-atomic antisymmetry in the spectral-product representation of Eq. (3) and the condition $\mathbf{S}(\boldsymbol{R}\to\infty)\to\mathbf{I}$ insures that well-defined Hermitian representatives $\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R})$ and $\mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})$ of the atomic and interaction-energy operators of Eqs. (4) and (5), respectively, are obtained which *individually* have appropriate asymptotic-separation limits, providing the correct atomic-product aggregate eigenstates and the associated sums of atomic energies in Eq. (12) in this limit. By contrast, an explicitly antisymmetrized basis $\hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R})$ does not allow for the definition of individual atomic and atomic-interaction operators and associated Hermitian matrix representatives from the expectation value of the aggregate Hamiltonian operator which *individually* have appropriate aggregate dissociation limits, the various potential energy terms contributing differently as intra- or inter-atomic interactions consequent of the different atomic assignments of electrons arising from the different permutations in the basis states.

Of course, the *total* Hamiltonian matrix in the antisymmetrized basis has a satisfactory dissociation limit ($\boldsymbol{R} \to \infty$), although this matrix is generally singular in the spectral closure limit consequent of the linear dependence of the overcomplete explicitly antisymmetrized basis at any finite $\boldsymbol{R}$ [12,20,22]. Additionally, the total or aggregate electron probability density matrices $\boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R})^\dagger \cdot \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R})$ and $\hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R})^\dagger \cdot \hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R})$ are identical in the limit $\boldsymbol{R} \to \infty$, insuring the distinguishability of the electrons assigned to the different atoms in this limit on basis of non-overlap of the atomic states employed, even in the presence of explicit antisymmetry [26]. This equivalence by itself, however, is insufficient to insure that the explicitly antisymmetric representation provides atomic and interaction operators and matrices which individually have appropriate asymptotic separation limits.

### 2.2 Atomic-Pair Transformation Formalism

The particularly simple forms of the atomic and interaction-energy terms appearing in the Hamiltonian matrix of Eq. (7) suggest the possibility of systematic evaluation of these component matrices in a series of individual atomic and atomic-pair calculations which can be performed once and for all independent of any particular atomic aggregate arrangement. Since atomic and diatomic eigenspectra are generally available from experimental and previous theoretical studies, the quality of the required calculations of component information can be critically evaluated in this approach through suitable comparisons prior to their incorporation in the spectral-product representation of Eqs. (1) to (12).

In order to explore the foregoing line of reasoning, it is helpful to write the Hamiltonian operator of Eq. (2) in the three alternative but equivalent forms [14]

$$\hat{H}(\boldsymbol{r}:\boldsymbol{R}) = \sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) - \frac{(N-2)}{(N-1)}\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}\to\infty)\Big\}$$

$$= \sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) - \frac{(N-2)}{(N-1)}\big(\hat{H}^{(\alpha)}(\boldsymbol{i})+\hat{H}^{(\beta)}(\boldsymbol{j})\big)\Big\}$$

$$= \sum_{\alpha=1}^{N}\Big\{\hat{H}^{(\alpha)}(\boldsymbol{i}) + \sum_{\beta=\alpha+1}^{N}\big\{\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) - \hat{H}^{(\alpha)}(\boldsymbol{i}) - \hat{H}^{(\beta)}(\boldsymbol{j})\big\}\Big\}, \tag{13}$$

where

$$\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) \equiv \hat{H}^{(\alpha)}(\boldsymbol{i}) + \hat{H}^{(\beta)}(\boldsymbol{j}) + \hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) \tag{14}$$

is the diatomic Hamiltonian operator for atoms $\alpha$ and $\beta$. The operator of Eq. (14) is a symmetric function of electron coordinates $\boldsymbol{i}$ and $\boldsymbol{j}$, and, accordingly, has a physically significant Hermitian matrix representative in the spectral-product basis, whereas the interaction operator $\hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})$ of Eq. (5) is not a symmetric function of electron coordinates and, consequently, has no physical significance [27].

Employing Eq. (13), the Hamiltonian matrix of Eq. (7) can be written in the three corresponding equivalent forms

$$\mathbf{H}(\boldsymbol{R}) = \sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) - \frac{(N-2)}{(N-1)}\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}\to\infty)\Big\}$$

$$= \sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) - \frac{(N-2)}{(N-1)}\big\{\mathbf{H}^{(\alpha)}+\mathbf{H}^{(\beta)}\big\}\Big\}$$

$$= \sum_{\alpha=1}^{N}\Big\{\mathbf{H}^{(\alpha)} + \sum_{\beta=\alpha+1}^{N}\big\{\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) - \mathbf{H}^{(\alpha)} - \mathbf{H}^{(\beta)}\big\}\Big\}, \tag{15}$$

where the terms in the double sum in the last line define the $(\alpha,\beta)$ interaction potential matrices through the expression [cf., Eq. (14)]

$$\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \equiv \langle\mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle$$

$$= \mathbf{H}^{(\alpha)} + \mathbf{H}^{(\beta)} + \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}). \tag{16}$$

Although the diatomic matrix of Eq. (16) as written has the dimension of the entire spectral-product basis of Eq. (3), it is, of course, determined by the diatomic submatrix constructed from integrals over the subspace of atomic-pair functions $\mathbf{\Phi}^{(\alpha)}(\boldsymbol{i}) \otimes \mathbf{\Phi}^{(\beta)}(\boldsymbol{j})$ in which the diatomic operator of Eq. (14) acts, and by the outer product of this submatrix with the unit matrices expressing the orthonormality of the remaining $N-2$ atomic spectral basis states of Eq. (3). Moreover, in view of the ordering convention of Eq. (3), the matrices $\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ for the different atomic pairs are each differently arranged in terms of their atomic and pair-interaction matrix elements [8,12].

The transformed Hamiltonian matrix of Eq. (8) in the permutation-symmetry-adapted basis of Eq. (11) takes the three equivalent forms

$$\begin{aligned}
\mathbf{H}_{\mathbf{S}}(\boldsymbol{R}) &= \sum_{\alpha=1}^{N} \sum_{\beta=\alpha+1}^{N} \Big\{ \mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) - \frac{(N-2)}{(N-1)} \mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R} : \boldsymbol{R}_{\alpha\beta} \to \infty) \Big\} \\
&= \sum_{\alpha=1}^{N} \sum_{\beta=\alpha+1}^{N} \Big\{ \mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) - \frac{(N-2)}{(N-1)} \{ \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R}) \} \Big\} \\
&= \sum_{\alpha=1}^{N} \Big\{ \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) + \sum_{\beta=\alpha+1}^{N} \{ \mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) - \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) - \mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R}) \} \Big\}, \qquad (17)
\end{aligned}$$

where, as in Eq. (15), the terms in brackets in the last line define the $(\alpha, \beta)$ interaction matrices $\mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})$ through the expression [cf., Eqs. (8) and (16)]

$$\begin{aligned}
\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) &\equiv \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R}) \\
&= \langle \mathbf{\Phi}_{\mathbf{S}}(\boldsymbol{r} : \boldsymbol{R}) | \hat{H}^{(\alpha,\beta)}(\boldsymbol{i}, \boldsymbol{j} : \boldsymbol{R}_{\alpha\beta}) | \mathbf{\Phi}_{\mathbf{S}}(\boldsymbol{r} : \boldsymbol{R}) \rangle \\
&= \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R}) + \mathbf{V}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) \qquad (18)
\end{aligned}$$

for the corresponding transformed diatomic Hamiltonian matrix. The notation employed in the second term in the first lines of Eq. (17) means that the limit $\boldsymbol{R}_{\alpha\beta} \to \infty$ is to be taken in the operator $\hat{H}^{(\alpha,\beta)}(\boldsymbol{i}, \boldsymbol{j} : \boldsymbol{R}_{\alpha\beta})$ and in the matrix $\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$, but not in the functions $\mathbf{\Phi}_{\mathbf{S}}(\boldsymbol{r} : \boldsymbol{R})$ or the transformation matrix $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ in Eq. (18). Accordingly, with this convention the second term is seen to reduce correctly to the indicated sum of transformed atomic Hamiltonian matrices required to cancel the additional atomic terms included in the first double sum over atomic pairs, as in Eq. (15).

The diatomic Hamiltonian matrix of Eq. (18) is seen to include modifications of the corresponding bare diatomic matrix of Eq. (16) due to the inter-atomic antisymmetry required upon immersion of the interacting atomic pair in the molecular aggregate, accomplished through the action of the transformation matrix $\mathbf{U_S}(\boldsymbol{R})$ of Eq. (9). Accordingly, Eqs. (17) and (18) can provide an exact representation of the entire aggregate Hamiltonian matrix in the limit of closure in the form of sums of Hermitian atomic and atomic-pair-interaction matrices which individually have appropriate dissociation limits. In employing these expressions in computational applications, it is convenient to first perform an eigenvalue decomposition of the bare Hamiltonian matrix of Eq. (16) and to retain the eigenstates and energies so obtained for subsequent aggregate applications, rather than to retain the diatomic Hamiltonian matrix itself. In this way, as will be seen below, conventional computational methods can be brought to bear most conveniently in evaluations of the aggregate Hamiltonian matrix of Eqs. (15) to (18).

Incorporation of diatomic fragment information in the foregoing exact atomic-pair expressions as an alternative to direct evaluation of the interaction terms in the aggregate Hamiltonian matrix of Eqs. (7) and (8) is complicated by a number of issues. First, diatomic calculations are most conveniently performed in collinear coordinate systems having their $z$-axes, for example, aligned and employed as a common axis of quantization, rather than in the commonly-oriented coordinate systems describing the individual atoms $\alpha$ and $\beta$ in the aggregate laboratory coordinate frame. Second, the spectral-product basis of Eq. (3) will generally span unphysical states of the diatomic Hamiltonian operator of Eq. (14), suggesting that the spectrum of the Hamiltonian matrix of Eq. (16) will include both physical and non-Pauli eigensolutions, both of which can potentially contribute to the development. Third, the transformations expressing the aggregate Hamiltonian matrix in terms of its component diatomic parts require construction in the absence of any possible ambiguity or inconsistency which might preclude applications of the method as a convergent *ab initio* computational approach.

### 2.2.1 Spatial Frame Transformation

To accomplish the transformation from aggregate to diatomic frame, a row vector of spectral-product functions is constructed from Eq. (3) in which the two row vectors of atomic eigenstates $\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i})$ and $\boldsymbol{\Phi}^{(\beta)}(\boldsymbol{j})$ are transformed to eigenstates quantized in and functions of a co-aligned $z$-axis coordinate system in which diatomic calculations are conveniently performed, with all other functions unchanged [28],

$$\begin{aligned}\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d:\boldsymbol{R}) &= \left\{\boldsymbol{\Phi}^{(1)}(\boldsymbol{1})\otimes\cdots\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha)}(\boldsymbol{i}_d)\otimes\cdots\boldsymbol{\Phi}_{\mathbf{D}}^{(\beta)}(\boldsymbol{j}_d)\otimes\cdots\boldsymbol{\Phi}^{(N)}(\boldsymbol{n})\right\}_O \\ &= \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\cdot\left\{\mathbf{I}^{(1)}\otimes\cdots\mathbf{D}^{(\alpha)}(\hat{\boldsymbol{R}}_{\alpha\beta})^\dagger\otimes\cdots\mathbf{D}^{(\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})^\dagger\otimes\cdots\mathbf{I}^{(N)}\right\}_O \\ &\equiv \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\cdot\mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})^\dagger.\end{aligned} \tag{19}$$

Here, $\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha)}(\boldsymbol{i}_d)=\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i})\cdot\mathbf{D}^{(\alpha)}(\hat{\boldsymbol{R}}_{\alpha\beta})^\dagger$ and $\boldsymbol{\Phi}_{\mathbf{D}}^{(\beta)}(\boldsymbol{j}_d)=\boldsymbol{\Phi}^{(\beta)}(\boldsymbol{j})\cdot\mathbf{D}^{(\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})^\dagger$ are the $(\alpha,\beta)$ atomic spectral states in the diatomic frame, $\mathbf{D}^{(\alpha)}(\hat{\boldsymbol{R}}_{\alpha\beta})$ and $\mathbf{D}^{(\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})$ are matrices comprising appropriately ordered sets of rotation matrices for all of the multiplet eigenstates of the atoms $\alpha$ and $\beta$, respectively, the Euler angles $\hat{\boldsymbol{R}}_{\alpha\beta}$ are given by the polar angles $(\phi_{\alpha\beta},\theta_{\alpha\beta},0)$ specifying the direction of atom $\beta$ from $\alpha$ in the laboratory frame [16], and the matrix $\mathbf{D}^{(\alpha\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})$ defined by Eq. (19) is expressed as an appropriately ordered outer product of the two sets of atomic rotation matrices and unit matrices ($\mathbf{I}^{(\gamma)}$) for the other $N$-2 atoms [8]. The notation $\boldsymbol{r}_d$ employed in $\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d:\boldsymbol{R})$, and in related functions defined below, is meant to indicate a change of angular coordinates ($\phi_d=\phi-\phi_{\alpha\beta}$, $\theta_d=\theta-\theta_{\alpha\beta}$) only for those electrons ($\boldsymbol{i},\boldsymbol{j}\rightarrow\boldsymbol{i}_d,\boldsymbol{j}_d$) assigned to the atoms $(\alpha,\beta)$ whose eigenstates have been transformed to the diatomic coordinate frame, with the other $n_t-n_\alpha-n_\beta$ electron coordinates and $N-2$ row vectors of atomic states represented in the laboratory frame.

Transformation of the diatomic Hamiltonian of Eq. (16) to the basis of Eq. (19) provides the representation

$$\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})=\mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})^\dagger\cdot\mathbf{H}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta})\cdot\mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta}), \tag{20}$$

where the diatomic Hamiltonian matrix

$$\mathbf{H}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta})\equiv\langle\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d:\boldsymbol{R})|\hat{H}^{(\alpha,\beta)}(\boldsymbol{i}_d,\boldsymbol{j}_d:R_{\alpha\beta})|\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d:\boldsymbol{R})\rangle \tag{21}$$

depends by construction only on the scalar separation $R_{\alpha\beta}$. That is, the calculations implied by Eq. (21) are performed in the co-aligned diatomic coordinate systems in which the scalar $R_{\alpha\beta}$ specifies the separation of the atoms $\alpha$ and $\beta$ along the common $z$-axis.

### 2.2.2 Diatomic Subspace Representations

The physical and unphysical blocks of the Hamiltonian of Eq. (21) can be isolated following a development similar to that of Eqs. (8) to (11). In this diatomic case, however, transformation to a permutation-symmetry-adapted representation is required only in the subspace of product functions $\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha)}(\boldsymbol{i}_d) \otimes \boldsymbol{\Phi}_{\mathbf{D}}^{(\beta)}(\boldsymbol{j}_d)$ associated with the atoms $(\alpha, \beta)$ in which the diatomic Hamiltonian of Eq. (14) acts, although it is convenient to continue to write out all matrices in the dimensions of the full spectral-product basis of Eq. (3). Following this convention, the unitary transformation [cf., Eq. (8)]

$$\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \equiv \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger} \cdot \mathbf{H}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$$

$$= \begin{pmatrix} \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp} & \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pu} \\ \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{up} & \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{uu} \end{pmatrix}_{O} \rightarrow \begin{pmatrix} \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp} & \mathbf{0} \\ \mathbf{0} & \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{uu} \end{pmatrix}_{O} \tag{22}$$

is employed to isolate the physical and unphysical blocks of the diatomic Hamiltonian in the co-aligned coordinate frame, where $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ is the unitary matrix obtained from the diagonalization [cf., Eqs. (9) and (10)]

$$\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger} \cdot \mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) = \mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta})$$

$$= \begin{pmatrix} \{\mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp} & \mathbf{0} \\ \mathbf{0} & \{\mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{uu} \end{pmatrix}_{O} \rightarrow \begin{pmatrix} Q^{(\alpha,\beta)}\mathbf{I}_{pp} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}_{O} \tag{23}$$

of the Hermitian matrix representative of the atomic-pair antisymmetrizer in the spectral-product basis of Eq. (19),

$$\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) \equiv (Q^{(\alpha,\beta)})^{1/2} \langle \boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) | \hat{P}_{A}^{(\alpha,\beta)} | \boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \rangle$$

$$= \langle \hat{P}_{A}^{(\alpha,\beta)} \boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) | \hat{P}_{A}^{(\alpha,\beta)} \boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \rangle. \tag{24}$$

The asymptotically wave-function-normalized antisymmetrizer employed in Eqs. (23) and (24), $\hat{P}_{A}^{(\alpha,\beta)} = ((n_\alpha + n_\beta)!)^{-1/2}(n_\alpha! n_\beta!)^{-1/2} \sum_{p=i_d,j_d} (-1)^{\delta_p} \hat{P}_p$, operates only on electrons in the sets $\boldsymbol{i}_d$ and $\boldsymbol{j}_d$, the metric matrix $\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta})$ depends explicitly on $R_{\alpha\beta}$ through the overlap of the two sets of atomic eigenstates on atoms $\alpha$ and $\beta$, the value of the redundancy factor $Q^{(\alpha,\beta)} = (n_\alpha + n_\beta)!/(n_\alpha! n_\beta!)$ of the explicitly antisymmetrized basis $\hat{P}_A^{(\alpha,\beta)} \mathbf{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})$ follows from wave-function normalization of the antisymmetrizer, and $\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta} \to \infty) \to \mathbf{I}$ in the diatomic dissociation limit. As in Eq. (9), those eigenvalues in the diagonal matrix $\mathbf{S}_d^{(\alpha,\beta)}(R_{\alpha\beta})$ which approach $Q^{(\alpha,\beta)}$ are ordered in decreasing value along the upper diagonal and those that approach zero are placed in the lower diagonal, with the corresponding eigenvectors of the $\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta})$ matrix appearing in appropriate columns of the transformation matrix $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ of Eq. (23).

Of course, the expressions of Eqs. (22) to (24) include the matrix element re-arrangements required to enforce the ordering convention of Eq. (3), signified by the indicated subscripts, resulting in matrices which disguise the blocked structures of the explicit expressions given above [8,12]. That is, although the eigenvalues of the metric matrix of Eq. (24) can be ordered as indicated above in matrices representing the diatomic subspace of the spectral-product basis, their positions in the matrices of Eq. (23) must be in accordance with the particular ordering convention adopted in Eq. (3). Similarly, the energy matrix of Eq. (22) will not exhibit the explicitly blocked structure shown there after the matrix elements have been re-ordered in compliance with the ordering convention of Eq. (3).

States of totally-antisymmetric and non-totally-antisymmetric permutation symmetry in electron coordinates $\boldsymbol{i}_d$ and $\boldsymbol{j}_d$ defining the diatomic Hamiltonian matrix $\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ of Eq. (22) take the partitioned form [cf., Eq. (11)]

$$\begin{aligned}
\mathbf{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) &\equiv \mathbf{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \\
&= \mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})^\dagger \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \\
&\to \big\{\{\mathbf{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_p, \{\mathbf{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_u\big\}_O,
\end{aligned} \tag{25}$$

where Eq. (19) has been employed in the second line and closure implied in the last line. Finally, the dimensions of the physical subspaces defined in Eqs. (22) to (25) for the different atomic pairs can generally differ from one another and from the dimension of the aggregate physical subspace of Eq. (11), as is further clarified in Section 2.3 below.

### 2.2.3 Diatomic Eigenspectra

The eigenstates and energies of the partitioned diatomic Hamiltonian of Eq. (22) are obtained in the usual way from solution of

$$\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) = \mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta}), \tag{26}$$

where the diagonal eigenvalue matrix

$$\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta}) = \begin{pmatrix} \{\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp} & \mathbf{0} \\ \mathbf{0} & \{\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{uu} \end{pmatrix}_O \tag{27}$$

and the unitary transformation matrix

$$\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) = \begin{pmatrix} \{\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp} & \mathbf{0} \\ \mathbf{0} & \{\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{uu} \end{pmatrix}_O \tag{28}$$

comprising the diatomic eigenvectors are block diagonal by construction. The associated diatomic eigenstates take the partitioned form

$$\begin{aligned} \boldsymbol{\Psi}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) &\equiv \boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) \\ &= \boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) \\ &= \boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})^{\dagger} \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) \\ &\to \big\{\{\boldsymbol{\Psi}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_p, \{\boldsymbol{\Psi}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_u\big\}_O, \end{aligned} \tag{29}$$

consequent of Eqs. (25) to (28). Following the standard convention [17], the eigenvalues of the physical and unphysical blocks of Eq. (27) are ordered in increasing value down the diagonals, and the associated eigenstates of Eq. (29) are correspondingly ordered by appropriate arrangement of the columns of the two blocks of the transformation matrix of Eq. (28). As in Eqs. (22) to (24), the arrangement of elements in Eqs. (27) to (29) are brought in compliance with the indicated ordering convention, disguising the blocked natures of these expressions but not eliminating them.

Equations (26) to (29) complete the connection between the diatomic eigenstates and the aggregate spectral-product states, with the three transformation matrices in Eq. (29)

required to relate the two representations. The transformation matrix $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ of Eq. (23), obtained from the metric matrix of Eq. (24), and the matrices $\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta})$ and $\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta})$ of Eqs. (26) to (28) must be constructed individually for all contributing atomic pairs in order to implement the present development. These matrices depend only on the scalar separation $R_{\alpha\beta}$ and require diatomic calculations which are performed once and for all over a suitable range of interatomic separations, whereas the transformations of Eqs. (19) and (20) involve only the known universal Wigner D functions and can be evaluated employing a variety of available methods [29].

### 2.3 Atomic-Pair Aggregate Hamiltonian Matrix

When the atomic and diatomic information of the preceeding Section 2.2 is available from previous calculations, the development of the Eqs. (19) to (29) can be inverted to give

$$\begin{aligned}\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) &\equiv \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger}\cdot\mathbf{H}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\cdot\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\\ &= \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})^{\dagger}\cdot\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\cdot\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) \qquad (30)\end{aligned}$$

for the diatomic Hamiltonian matrix of Eq. (18), where $\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ obtained from Eqs. (26) to (28) is block diagonal by construction and the transformation matrix

$$\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) \equiv \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger}\cdot\mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})\cdot\mathbf{U}_{\mathbf{S}}(\boldsymbol{R}) \rightarrow \langle\boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d:\boldsymbol{R})|\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R})\rangle \qquad (31)$$

defined by Eq. (30) is the product of the three indicated transformation matrices. Each of the latter matrices has the dimension of the full spectral-product basis, with the indicated limiting expression obtained employing the definitions of Eqs. (11), (19), and (25) and summing over the formally complete intermediate states.

The closure limit of Eq. (31) demonstrates that the matrix $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})$ has a zero block in its lower left-hand corner, $\{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{up} = \mathbf{0}$, since $\{\boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d:\boldsymbol{R})\}_u$ of Eq. (25) is non-totally antisymmetric in electrons in the sets $\boldsymbol{i}_d$ and $\boldsymbol{j}_d$ and $\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r}:\boldsymbol{R})\}_p$ of Eq. (11) is totally antisymmetric in all electrons in this limit. This circumstance is sufficient to insure that the upper left-hand block $\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp}$ of Eq. (30) requires for its construction only the physical blocks of the diatomic energy and transformation matices of Eqs. (27) and

(28), and of the transformation matrix $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})$ of Eq. (31), with contributions from the unphysical and off-diagonal blocks of these latter matrices vanishing in the closure limit.

In light of the foregoing, the unphysical diatomic solutions of Eqs. (26) to (28) are not required in constructing the physical block of the aggregate Hamiltonian matrix of Eq. (17), which can be written in the three equivalent forms

$$\begin{aligned}
\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} &= \sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} - \frac{(N-2)}{(N-1)}\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R} : R_{\alpha\beta}\to\infty)\}_{pp}\Big\} \\
&= \sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} - \frac{(N-2)}{(N-1)}\big\{\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R})\big\}_{pp}\Big\} \\
&= \sum_{\alpha=1}^{N}\Big\{\{\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R})\}_{pp} + \sum_{\beta=\alpha+1}^{N}\big\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) - \mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) - \mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R})\big\}_{pp}\Big\},
\end{aligned} \tag{32}$$

where the physical block of the diatomic Hamiltonian matrix obtained from Eqs. (30) and (31) is

$$\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} = \{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp}^{\dagger}\cdot\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}\cdot\{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp}. \tag{33}$$

Equations (32) and (33) make clear that the dimensions of the physical subspace vectors $\{\boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_p$ and the square physical blocks of the atomic-pair Hamiltonian matrices $\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}$ can generally be different for the different atomic pairs, and that they can also differ from the dimension of the physical subspace $\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r} : \boldsymbol{R})\}_p$ of the aggregate representation of Eq. (11). Accordingly, the transformation matrices $\{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp}$ obtained from Eq. (31) are generally rectangular, with dimensions appropriate to the indicated matrix multiplications of Eq. (33), the final matrices $\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp}$ all having the dimension of the physical subspace of Eq. (11).

The notation employed in the second term in the first line of Eq. (32) implies that the scalar limit $R_{\alpha\beta}\to\infty$ is to be taken in all matrices in Eqs. (30), (31), and (33) except the transformation matrix $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$. Accordingly, this second term is seen to reduce correctly to the indicated sum of atomic Hamiltonian matrices required to cancel the additional atomic terms included in the first double sum over atomic pairs. Specifically, employing the limits $\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta}\to\infty)\to\mathbf{H}^{(\alpha)}+\mathbf{H}^{(\beta)}$ and $\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}\to\infty)\to\mathbf{I}$ in Eq. (33), and noting that $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta} \to \infty) \to \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\infty)$ in Eq. (31), gives $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) \to \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\infty) \cdot \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$. Finally, noting that $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\infty)$ will only include off-diagonal terms which correspond to admixtures of degenerate states in the sum of matrices $\mathbf{H}^{(\alpha)}$ and $\mathbf{H}^{(\beta)}$ by construction, and employing the commutation of $\mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})$ with the atomic energy matrices $\mathbf{H}^{(\alpha)}$ and $\mathbf{H}^{(\beta)}$ consequent of the well-known energy degeneracy of atomic multiplet states [18], demonstrates the equivalence of the three forms of the Hamiltonian matrix given in Eq. (32).

Equation (32) and the associated transformations of Eqs. (30), (31), and (33) provide a formally exact expression for the Hamiltonian matrix of a molecule or other finite atomic aggregate in terms of atomic and diatomic energies which can be determined once and for all from appropriate separate calulations. The metric and transformation matrices of Eqs. (9) and (10) are the only factors in the development that refer explicitly to the particular spatial arrangement of the interacting atomic constituents. These provide the modifications of the bare atomic energies and diatomic interaction energies due to the inter-atomic aggregate electron antisymmetry required upon their incorporation in the larger aggregate, and must be determined separately for each individual atomic arrangement considered. Since aggregate electron antisymmetry is expressed in the present development through the $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ matrix, rather than as an *ad hoc* global constraint, accurate evaluations of the interaction Hamiltonian of Eq. (33) may be obtained in some cases by including only small numbers of atoms in near proximity to a given interacting pair in construction of the required metric and transformation matrices. More generally, essentially complete evaluations of the aggregate metric matrix can be performed from the one-electron orbital overlap integrals in which it can ultimately be expressed, and the associated unitary transformation matrix obtained from Eq. (9).

The atomic and diatomic calculations required in constructing Eqs. (32) and (33) are performed variationally, insuring that the resulting atomic energies and potential energy curves provide upper bounds to the corresponding energies obtained from exact solutions of the associated atomic and diatomic Schrödinger equations. These calculations fix the dimensions of the physical vectors $\{\boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_p$ appearing in Eq. (31) and of the physical blocks $\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}$ of the diatomic interaction Hamiltonian matrices appearing in Eq. (33), but not necessarily that of the dimension of the aggregate physical vector $\{\mathbf{\Phi}_{\mathbf{S}}(\boldsymbol{r} : \boldsymbol{R})\}_p$ in Eq. (31). Accordingly, as the dimension of the latter representation is increased for fixed dimensions of the diatomic subspaces, bounded (Hylleraas-Undheim) convergence is obtained to the aggregate energies defined by the chosen diatomic representations. Of course, this does not insure that the aggregate energies obtained in this manner will provide upper bounds to those energies obtained from exact solutions of the Schrödinger equation of Eq. (1). Nevertheless, it can be anticipated that reliable results can be obtained from the development for specific aggregate states when sufficiently converged representations are achieved for the corresponding bare diatomic states, issues which must be addressed in the course of computational implementations and specific applications.

## 3.0 Illustrative Computational Implementation

A particular computational implementation of the foregoing development is provided in Section 3.1 employing valence-bond methods in constructing atomic and diatomic information, explicit closure limits of the aggregate spectral-product representation in completing the evaluation of the exact-pair expressions of Eqs. (32) and (33) are described in Section 3.2, and an illustrative computational application to the $H_3$ molecule is reported in Section 3.3.

## 3.1 Calculations of Atomic and Diatomic Information

The diatomic information required in evaluation of the matrices of Eqs. (30) to (33), although formally defined in the spectral-product representation, can be obtained employing explicitly antisymmetrized valence-bond methods [5]. This is conveniently accomplished in the present implementation by construction of an explicitly antisymmetric form of the permutation-symmetry-adapted diatomic subspace $\mathbf{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : R_{\alpha\beta})$ of Eq. (25). Specifically required for this purpose, in addition to the atomic eigenstates $\mathbf{\Phi}^{(\alpha)}(\boldsymbol{i})$ and energy matrices $\mathbf{H}^{(\alpha)}$, are the diatomic matrices $\mathbf{S}^{(\alpha,\beta)}(R_{\alpha\beta})$, $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ and the diatomic eigenspectra $\{\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}$, $\{\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}$ of Sections 2.2.2 and 2.2.3 obtained from the Hamiltonian matrix $\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}$, all of which information is provided by suitable processing of the results of explicitly antisymmetric valence-bond calculations incorporated into the spectral-product development.

Sets of orthonormal antisymmetric atomic configurational state functions $\tilde{\boldsymbol{\Phi}}^{(\alpha)}(\boldsymbol{i})$, chosen in the form of Slater determinants of canonical Hartree-Fock orbitals, are employed in construction of the required row vectors of atomic spectral eigenfunctions $\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i}) = \tilde{\boldsymbol{\Phi}}^{(\alpha)}(\boldsymbol{i}) \cdot \widetilde{\mathbf{M}}^{(\alpha)}$. Here, the matrix $\widetilde{\mathbf{M}}^{(\alpha)}$ is obtained from diagonalization of the atomic Hamiltonian matrix $\langle \tilde{\boldsymbol{\Phi}}^{(\alpha)}(\boldsymbol{i}) | \hat{H}^{(\alpha)}(\boldsymbol{i}) | \tilde{\boldsymbol{\Phi}}^{(\alpha)}(\boldsymbol{i}) \rangle$ constructed in the orthonormal basis $\tilde{\boldsymbol{\Phi}}^{(\alpha)}(\boldsymbol{i})$, which calculations also provide the atomic energy matrices $\mathbf{H}^{(\alpha)}$ of Eq. (7). The aggregate atomic spectral-product basis of Eq. (3) is obtained in this way in the form $\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) = \tilde{\boldsymbol{\Phi}}(\boldsymbol{r}:\boldsymbol{R}) \cdot \widetilde{\mathbf{M}}$, where [cf., Eq. (3)]

$$\tilde{\boldsymbol{\Phi}}(\boldsymbol{r}:\boldsymbol{R}) = \left\{ \tilde{\boldsymbol{\Phi}}^{(1)}(\boldsymbol{1}) \otimes \tilde{\boldsymbol{\Phi}}^{(2)}(\boldsymbol{2}) \otimes \cdots \tilde{\boldsymbol{\Phi}}^{(N)}(\boldsymbol{n}) \right\}_O \tag{34}$$

is the spectral product of atomic configurational state functions and the matrix $\widetilde{\mathbf{M}}$ is given by the outer matrix product

$$\widetilde{\mathbf{M}} = \left\{ \widetilde{\mathbf{M}}^{(1)} \otimes \widetilde{\mathbf{M}}^{(2)} \otimes \cdots \widetilde{\mathbf{M}}^{(N)} \right\}_O . \tag{35}$$

Similarly, the $(\alpha,\beta)$ metric matrix of Eq. (24) is obtained in the form

$$\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) = \widetilde{\mathbf{M}}^{(\alpha,\beta)\dagger} \cdot \widetilde{\mathbf{S}}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \widetilde{\mathbf{M}}^{(\alpha,\beta)}, \tag{36}$$

where $\widetilde{\mathbf{M}}^{(\alpha,\beta)}$ is the outer matrix product [cf., Eq. (35)]

$$\widetilde{\mathbf{M}}^{(\alpha,\beta)} \equiv \left\{ \mathbf{I}^{(1)} \otimes \cdots \widetilde{\mathbf{M}}^{(\alpha)} \otimes \cdots \widetilde{\mathbf{M}}^{(\beta)} \otimes \cdots \mathbf{I}^{(N)} \right\}_O . \tag{37}$$

The metric matrix $\widetilde{\mathbf{S}}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta)}) = (Q^{(\alpha,\beta)})^{1/2} \langle \tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) | \hat{P}_A^{(\alpha,\beta)} | \tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \rangle$ is obtained from valence-bond calculations of the states [cf., Eq. (19)]

$$\tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) = \left\{ \tilde{\boldsymbol{\Phi}}^{(1)}(\boldsymbol{1}) \otimes \cdots \tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\alpha)}(\boldsymbol{i}_d) \otimes \cdots \tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\beta)}(\boldsymbol{j}_d) \otimes \cdots \tilde{\boldsymbol{\Phi}}^{(N)}(\boldsymbol{n}) \right\}_O \tag{38}$$

employing Eq. (34) and the indicated atomic spectral substitutions. The information of Eqs. (34) to (38), when employed in the development of Eqs. (22) to (24) providing the unitary transformation matrix $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ and eigenvalues $\mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta})$, gives the physical block of the diatomic Hamiltonian matrix of Eq. (22) in the familiar form [11,12]

$$\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp} =$$

$$\{\mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}^{-1/2} \cdot \{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger} \cdot \mathbf{H}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp} \cdot \{\mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}^{-1/2}. \quad (39)$$

Here, $\mathbf{H}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) = \widetilde{\mathbf{M}}^{(\alpha,\beta)\dagger} \cdot \widetilde{\mathbf{H}}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \widetilde{\mathbf{M}}^{(\alpha,\beta)}$ expresses the diatomic Hamiltonian matrix of Eq. (21) in terms of the corresponding matrix $\widetilde{\mathbf{H}}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta})$ constructed in the non-orthogonal valence-bond basis $\hat{P}_{A}^{(\alpha,\beta)}\tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})$, with $\tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})$ given by Eq. (38). Although the foregoing expressions are presented in the dimension of the aggregate spectral-product basis as a notational convenience, of course, only atomic and diatomic representations are required in the calculations performed.

Finally, it is seen from the development of Eqs. (34) to (39) that the physical diatomic subspace of Eq. (25) is obtained from the present implementation in the form

$$\begin{aligned}
\{\boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_p &\equiv \{\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_p \\
&= \{\hat{P}_{A}^{(\alpha,\beta)}\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_p \cdot \{\mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta})\}_{pp}^{-1/2} \\
&\rightarrow \{\hat{P}_{A}^{(\alpha,\beta)}\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})\}_p \; (Q^{(\alpha,\beta)})^{-1/2}, \qquad (40)
\end{aligned}$$

where the $\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta})$ and $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ matrices and the basis states $\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) = \tilde{\boldsymbol{\Phi}}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) \cdot \widetilde{\mathbf{M}}^{(\alpha,\beta)}$ are obtained from the foregoing expressions. Equations (34) to (40) are evidently sufficient to obtain the physical blocks of the diatomic energy and transformation matrices by the diagonalization of Eqs. (27) and (28), which completes determination of the specifically atomic and diatomic information required in constructing the atomic-pair interaction energy matrix of Eq. (33).

The role of the $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ matrix of Eq. (23) in the first line of Eq. (40) is to isolate the totally antisymmetric subspace of the $(\alpha, \beta)$ spectral-product representation in accordance with Eqs. (22) to (24) [11,12], whereas in the second and third lines the transformation provides a linearly-independent orthonormal subspace of the $Q^{(\alpha,\beta)}$-fold redundant, linearly-dependent, explicitly antisymmetrized $(\alpha, \beta)$ spectral-product basis

$\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}_{\mathbf{D}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})$ constructed following well-known canonical orthogonalization procedures [30]. Correspondingly, the spectral-product expression for $\{\boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_p$ in the first line in Eq. (40) converges to the indicated antisymmetric expression for diatomic separations $R_{\alpha\beta}$ at which the spectral closure limit is attained [11,12]. As a consequence, the equivalence between the spectral-product form and the explicitly antisymmetrized expressions of Eq. (39) can fail in the dissociation limit, when $\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta} \to \infty) \to \mathbf{I}$ rather than $\to Q^{(\alpha,\beta)}\mathbf{I}$, with the spectral-product representation of $\{\boldsymbol{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})\}_p$ dissociating to a product form and the explicitly antisymmetric expressions in the second and third lines of Eq. (40) remaining antisymmetric in the dissociation limit.

### 3.2 Aggregate Spectral-Product Closure Limits

Completion of construction of the Hamiltonian matrix of Eqs. (32) and (33) requires the aggregate physical subspace $\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r} : \boldsymbol{R})\}_p$ of Eq. (11) and the transformation matrix of Eq. (31). Following the development of Eqs. (34) to (40), the aggregate subspace is obtained in the form

$$\begin{aligned}
\{\boldsymbol{\Phi}_{\mathbf{S}}(\boldsymbol{r} : \boldsymbol{R})\}_p &\equiv \{\boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_p \\
&= \{\hat{P}_A\boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_p \cdot \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2} \\
&\to \{\hat{P}_A\boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_p \, Q^{-1/2},
\end{aligned} \tag{41}$$

which expressions have been shown to converge as indicated for all atomic arrangements $\boldsymbol{R}$ at which the limit of spectral closure is achieved [11,12]. Here, the aggregate basis $\boldsymbol{\Phi}(\boldsymbol{r} : \boldsymbol{R}) = \tilde{\boldsymbol{\Phi}}(\boldsymbol{r} : \boldsymbol{R}) \cdot \widetilde{\mathbf{M}}$ is obtained from Eqs. (34) and (35) and the transformation matrix $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ from Eqs. (9) and (10) employing the metric matrix constructed in the valence-bond representation, $\mathbf{S}(\boldsymbol{R}) = Q^{1/2}\widetilde{\mathbf{M}}^{\dagger} \cdot \langle\tilde{\boldsymbol{\Phi}}(\boldsymbol{r} : \boldsymbol{R})|\hat{P}_A|\tilde{\boldsymbol{\Phi}}(\boldsymbol{r} : \boldsymbol{R})\rangle \cdot \widetilde{\mathbf{M}}$. Although the second and third lines of Eq. (41) as written formally imply global enforcement of antisymmetry for all aggregate electrons, when the range of interactions in the Hamiltonian matrix of Eqs. (32) and (33) are sufficiently limited only small numbers of atoms in close spatial proximity to a given interacting pair will contribute significantly to the metric matrix $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ required for evaluation of Eq. (33), potentially simplifying the calculation. More generally, as indicated above, complete evaluation of the transformation matrix $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$ is accomplished from the one-electron overlap integrals which are required in the construction of the corresponding S-matrix.

The $\mathbf{U_S}(\boldsymbol{R})$ matrix in the first line of Eq. (41) isolates the totally antisymmetric subspace of the spectral-product representation, in accordance with Eqs. (8) to (11), whereas in the second and third lines it provides a linearly-independent orthonormal subspace of the $Q$-fold redundant, linearly-dependent, explicitly antisymmetrized spectral-product basis [11,12]. As in Eq. (40), the equivalence of the spectral-product expression in Eq. (41) with two explicitly antisymmetrized expressions given there can fail in the dissociation limit when $\mathbf{S}(\boldsymbol{R} \to \infty) \to \mathbf{I}$ rather than $\to Q\mathbf{I}$. Correspondingly, as indicated in the discussion of Eq. (12) above, the spectral-product representation of $\{\boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r} : \boldsymbol{R})\}_p$ in this case dissociates to a product form $[\boldsymbol{\Phi}(\boldsymbol{r} : \infty) \cdot \mathbf{U_S}(\infty)]$, whereas the expressions in the second and third lines of Eq. (41) remain explicitly antisymmetric in the dissociation limit in the form $\hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r} : \infty) \cdot \mathbf{U_S}(\infty)$.

Finally, employing Eqs. (40) and (41) in evaluating the physical block of the transformation matrix $\mathbf{U}_\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R})$ of Eq. (31) gives

$$\{\mathbf{U}_\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} \equiv \{\langle \boldsymbol{\Phi}_\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R}) | \boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r} : \boldsymbol{R})\rangle\}_{pp}$$

$$= \{\mathbf{S}_d^{(\alpha,\beta)}(R_{\alpha\beta})/Q^{(\alpha,\beta)}\}_{pp}^{-1/2} \cdot \{\mathbf{U}_\mathbf{S}^{(\alpha,\beta)}(R_{\alpha\beta})^\dagger \cdot \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta}) \cdot \mathbf{U_S}(\boldsymbol{R})\}_{pp} \cdot \{\mathbf{S}_d(\boldsymbol{R})/Q\}_{pp}^{1/2}$$

$$\to \{\mathbf{U}_\mathbf{S}^{(\alpha,\beta)}(R_{\alpha\beta})^\dagger \cdot \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta}) \cdot \mathbf{U_S}(\boldsymbol{R})\}_{pp}, \tag{42}$$

where the last line indicates the closure limit. The latter expression is evidently identical in appearance to the physical block of Eq. (31) constructed entirely in the spectral-product representation, in spite of the fact that Eq. (42) employs the explicitly antisymmetric diatomic and aggregate states of Eqs. (39) and (41). This equivalence is in accord with the recognition that any distinction between the physical subspace of the atomic spectral-product representation and the linearly-independent subspace of its explicitly antisymmetrized form must become inconsequential in the closure limit [11,12].

Although it can be expected that the explicitly antisymmetric expressions in Eqs. (40) and (41) will be more rapidly convergent with dimension of the basis than will be the expansions in the product basis itself, some care must be exercised in using the former expressions. Specifically, the aforementioned failure of equivalence between the spectral-product and explicitly antisymmetric representations in Eqs. (40) and (41) at arbitrarily large $R_{\alpha\beta}$ and $\boldsymbol{R}$ results in the second line of Eq. (42) having the dissociation limit $\{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R} \to \infty)\}_{pp} \to (Q^{(\alpha,\beta)}/Q)^{1/2}\{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\infty) \cdot \mathbf{U}_{\mathbf{S}}(\infty) \cdot \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})\}_{pp}$, which includes the apparently spurious factor $(Q^{(\alpha,\beta)}/Q)^{1/2}$. This factor would seem to modify the long-range behavior of the matrix $\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp}$ of Eq. (33), which has the apparent limit $\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R} \to \infty)\}_{pp} \to (Q^{(\alpha,\beta)}/Q)\ \mathbf{U}_{\mathbf{S}}(\infty)^{\dagger} \cdot \{\mathbf{H}^{(\alpha)} + \mathbf{H}^{(\beta)}\} \cdot \mathbf{U}_{\mathbf{S}}(\infty)$, causing Eq. (32) to violate the dissociation limit of Eq. (12). As a practical matter, however, the expressions implied by the last lines of Eqs. (40) to (42) can always be satisfied in large but finite spatial regions. Specifically, the spectral closure limits $\{\mathbf{S}_d^{(\alpha,\beta)}(R_{\alpha\beta} \leq R_{\alpha\beta}^{(\infty)})\}_{pp} \to Q^{(\alpha,\beta)}\mathbf{I}_{pp}$ can be satisfied for each atomic pair in the indicated intervals in suitably chosen denumerable $L^2$ diatomic representations, where the radii $R_{\alpha\beta}^{(\infty)}$ have sufficiently large but finite values such that the diatomic energy matrices in Eq. (33) take the limiting forms $\{\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta} \to R_{\alpha,\beta}^{(\infty)})\}_{pp} \to \mathbf{H}^{(\alpha)} + \mathbf{H}^{(\beta)}$. The spectral closure limit $\{\mathbf{S}_d(\boldsymbol{R} \leq \boldsymbol{R}_{\infty})\}_{pp} \to Q\mathbf{I}$ is correspondingly attained in the domain $\boldsymbol{R} \leq \boldsymbol{R}_{\infty}$ employing the aggregate basis states defined by at least the individual diatomic representations employed, where $\boldsymbol{R}_{\infty}$ is the union of the $R_{\alpha\beta}^{(\infty)}$ values for all atomic pairs. Under these conditions, the closure limits implied in the last lines of Eqs. (40) to (42) are satisfied and the aggregate Hamiltonian matrix $\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R}_{\infty})\}_{pp}$ of Eq. (32) can be correctly regarded as the sum of non-interacting atomic Hamiltonian matrices of Eq. (12).

### 3.3 Illustrative Computational Application

The doublet and quartet potential energy surfaces of the $H_3$ molecule are studied in a minimal ($1s^3$) basis [31] as an illustrative application of the particular implementation of the exact-pair formalism given in the foregoing Sections 3.1 and 3.2. Of course, closure limits are not achieved in this model representation, which provides only an illustration in which it is possible to write out in detail the various expressions devised, to demonstrate that sensible results can be obtained from the development employing even the smallest possible basis sets, and to aid comparisons with related semi-empirical approaches [13,14].

Restricting attention to $M_S = +1/2$ states of the $\mathrm{H}_3$ molecule, the spectral-product basis of Eq. (3) in this case takes the three-term form

$$\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) = \big\{\alpha(1)\alpha(2)\beta(3), \alpha(1)\beta(2)\alpha(3), \beta(1)\alpha(2)\alpha(3)\big\}1s_a(1)1s_b(2)1s_c(3), \tag{43}$$

where $\boldsymbol{r} \equiv (\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$, $\boldsymbol{R} \equiv (\boldsymbol{R}_a = \boldsymbol{0}, \boldsymbol{R}_b, \boldsymbol{R}_c)$, $\alpha(i)$ and $\beta(i)$ are the Pauli spin functions, and $1s_\alpha(i) \equiv 1s_\alpha(|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|)$ refers to the $1s$ orbital centered on atom $\alpha$. The metric matrix of Eq. (10) in this case is

$$\mathbf{S}(\boldsymbol{R}) = \begin{pmatrix} 1 - s_{ab}^2 & s_{ab}s_{ac}s_{bc} - s_{bc}^2 & s_{ab}s_{ac}s_{bc} - s_{ac}^2 \\ s_{ab}s_{ac}s_{bc} - s_{bc}^2 & 1 - s_{ac}^2 & s_{ab}s_{ac}s_{bc} - s_{ab}^2 \\ s_{ab}s_{ac}s_{bc} - s_{ac}^2 & s_{ab}s_{ac}s_{bc} - s_{ab}^2 & 1 - s_{bc}^2 \end{pmatrix}, \tag{44}$$

where $s_{\alpha\beta} = s(R_{\alpha\beta}) \equiv \langle 1s_\alpha(i)|1s_\beta(i)\rangle \le 1$ is the one-electron $1s$ orbital overlap integral, and the transformation matrix $\mathbf{U}_\mathbf{S}(\boldsymbol{R})$ and eigenvalue matrix $\mathbf{S}_d(\boldsymbol{R})$ are obtained from diagonalization of the metric matrix of Eq. (44) following the development of Eqs. (9) and (10). Specifically, the eigenvalues of the $\mathbf{S}(\boldsymbol{R})$ matrix are found to be

$$\{\mathbf{S}_d(\boldsymbol{R})\}_{1,2} = 1 - s_{ab}s_{bc}s_{ca} \pm \frac{1}{\sqrt{2}}\big\{(s_{ab}^2 - s_{ac}^2)^2 + (s_{ab}^2 - s_{bc}^2)^2 + (s_{ac}^2 - s_{bc}^2)^2\big\}^{1/2} \tag{45$a$}$$

$$\{\mathbf{S}_d(\boldsymbol{R})\}_3 = 1 - s_{ab}^2 - s_{ac}^2 - s_{bc}^2 + 2s_{ab}s_{bc}s_{ac}, \tag{45$b$}$$

and the corrersponding $\mathbf{U}_\mathbf{S}(\boldsymbol{R})$ matrix is

$$\mathbf{U}_\mathbf{S}(\boldsymbol{R}) = \begin{pmatrix} \frac{1}{\sqrt{6}}cos\Theta(\boldsymbol{R}) - \frac{1}{\sqrt{2}}sin\Theta(\boldsymbol{R}) & \frac{1}{\sqrt{6}}sin\Theta(\boldsymbol{R}) + \frac{1}{\sqrt{2}}cos\Theta(\boldsymbol{R}) & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{6}}cos\Theta(\boldsymbol{R}) + \frac{1}{\sqrt{2}}sin\Theta(\boldsymbol{R}) & \frac{1}{\sqrt{6}}sin\Theta(\boldsymbol{R}) - \frac{1}{\sqrt{2}}cos\Theta(\boldsymbol{R}) & \frac{1}{\sqrt{3}} \\ -\frac{2}{\sqrt{6}}cos\Theta(\boldsymbol{R}) & -\frac{2}{\sqrt{6}}sin\Theta(\boldsymbol{R}) & \frac{1}{\sqrt{3}} \end{pmatrix}, \tag{46$a$}$$

where

$$\Theta(\boldsymbol{R}) = \frac{1}{2}tan^{-1}\Big\{\frac{\sqrt{3}(s_{ab}^2 - s_{ac}^2)}{(s_{ab}^2 - 2s_{bc}^2 + s_{ac}^2)}\Big\}. \tag{46$b$}$$

The two eigenvalues given by Eq. (45a) and the first two columns of the matrix of Eq. (46a) correspond to doublet states, whereas Eq. (45b) and the last column of Eq. (46a) correspond to a quartet state. That is, the states $\boldsymbol{\Phi}_\mathbf{S}(\boldsymbol{r}:\boldsymbol{R})$ of Eqs. (11) and (41) in this example are $S$=1/2, 3/2; $M_S$=+1/2 spin multiplets, symmetries which are maintained in the three-atom dissociation limit, in which case $cos\Theta(\boldsymbol{R} \to \infty) \to 1$, $sin\Theta(\boldsymbol{R} \to \infty) \to 0$, and $\mathbf{U}_\mathbf{S}(\boldsymbol{R} \to \infty) \to \mathbf{U}_\mathbf{S}(\infty) \neq \mathbf{I}$. They are linearly-independent combinations of the antisymmetrized forms of the three-term basis of Eq. (43) when the corresponding eigenvalues of Eqs. (45) do not vanish.

The diatomic metric matrices $\mathbf{S}_{\mathbf{D}}^{(\alpha,\beta)}(R_{\alpha\beta})$ and the correrspondng transformation matrices $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ of Eqs. (23) and (24) are obtained in the forms

$$\mathbf{S}_{\mathbf{D}}^{(a,b)}(R_{ab}) = \begin{pmatrix} 1-s_{ab}^2 & 0 & 0 \\ 0 & 1 & -s_{ab}^2 \\ 0 & -s_{ab}^2 & 1 \end{pmatrix}, \quad \mathbf{U}_{\mathbf{S}}^{(a,b)}(R_{ab}) = \begin{pmatrix} 0 & 1 & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{pmatrix}, \tag{47$a$}$$

$$\mathbf{S}_{\mathbf{D}}^{(a,c)}(R_{ac}) = \begin{pmatrix} 1 & 0 & -s_{ac}^2 \\ 0 & 1-s_{ac}^2 & 0 \\ -s_{ac}^2 & 0 & 1 \end{pmatrix}, \quad \mathbf{U}_{\mathbf{S}}^{(a,c)}(R_{ac}) = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{pmatrix}, \tag{47$b$}$$

$$\mathbf{S}_{\mathbf{D}}^{(b,c)}(R_{bc}) = \begin{pmatrix} 1 & -s_{bc}^2 & 0 \\ -s_{bc}^2 & 1 & 0 \\ 0 & 0 & 1-s_{bc}^2 \end{pmatrix}, \quad \mathbf{U}_{\mathbf{S}}^{(b,c)}(R_{bc}) = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix}, \tag{47$c$}$$

with the eigenvalues of the three diatomic S-matrices all taking the identical form

$$\begin{aligned} \mathbf{S}_{d}^{(\alpha,\beta)}(R_{\alpha\beta}) &= \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger} \cdot \mathbf{S}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \\ &= \begin{pmatrix} 1+s_{\alpha\beta}^2 & 0 & 0 \\ 0 & 1-s_{\alpha\beta}^2 & 0 \\ 0 & 0 & 1-s_{\alpha\beta}^2 \end{pmatrix}. \end{aligned} \tag{47$d$}$$

Construction of the states $\mathbf{\Phi}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{r}_d : \boldsymbol{R})$ of Eqs. (25) and (40) employing the $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})$ matrices of Eqs. (47a) to (47c) shows them to be products of diatomic states ($ab$, $ac$, or $bc$) of ${}^1\Sigma_g^+$ or ${}^3\Sigma_u^+$ symmetry with a $1s$ atomic spin orbital ($c$, $b$, or $a$) of appropriate electron spin. That is, the transformations of Eqs. (25) and (40) provide the correct diatomic eigenstates for the three atomic pairs, so that the diatomic Hamiltonian matrices of Eqs. (22) and (39) are diagonal and $\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) = \mathbf{I}$ for all three pairs in this example. The diagonal diatomic energy matrix $\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta})$ of Eq. (27) is the same for all three diatomic pairs in this case and takes the form

$$\mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta}) = \begin{pmatrix} {}^1E(R_{\alpha\beta}) & 0 & 0 \\ 0 & {}^3E(R_{\alpha\beta}) & 0 \\ 0 & 0 & {}^3E(R_{\alpha\beta}) \end{pmatrix}, \tag{48}$$

where ${}^{1,3}E(R_{\alpha\beta})$ refer to the singlet and triplet Heitler-London $H_2$ energy curves.

The aggregate atomic-pair Hamiltonian matrix of Eq. (17) in this case is

$$\begin{aligned}
\mathbf{H}_{\mathbf{S}}(\boldsymbol{R}) &= \mathbf{H}_{\mathbf{S}}^{(a,b)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(a,c)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(b,c)}(\boldsymbol{R}) - \left\{\mathbf{H}_{\mathbf{S}}^{(a)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(b)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(c)}(\boldsymbol{R})\right\} \\
&= \mathbf{H}_{\mathbf{S}}^{(a,b)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(a,c)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(b,c)}(\boldsymbol{R}) - 3E_{1s}\mathbf{I} \\
&= 3E_{1s}\mathbf{I} + \{\mathbf{H}_{\mathbf{S}}^{(a,b)}(\boldsymbol{R}) - 2E_{1s}\mathbf{I}\} + \{\mathbf{H}_{\mathbf{S}}^{(a,c)}(\boldsymbol{R}) - 2E_{1s}\mathbf{I}\} + \{\mathbf{H}_{\mathbf{S}}^{(b,c)}(\boldsymbol{R}) - 2E_{1s}\mathbf{I}\},
\end{aligned} \tag{49}$$

where $E_{1s}$ is the $1s$ orbital energy and the diatomic pair terms of Eqs. (30), (31), and (33),

$$\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}) = \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{E}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger} \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R}), \tag{50}$$

are constructed from Eqs. (39) to (42). Note that $\mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta}) = \mathbf{I}$ in Eqs. (49) and (50), since only $1s$ orbitals are employed, $\mathbf{U}_{\mathbf{H}}^{(\alpha,\beta)}(R_{\alpha\beta}) = \mathbf{I}$ since the correct Heitler-London ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ wave functions are obtained from the permutation-symmetry-adapted diatomic states of Eqs. (25) and (40) in this case, and the last two lines in Eq. (49) follow from the commutation of the three atomic Hamiltonian matrices ($\mathbf{H}^{(\alpha)} = E_{1s}\mathbf{I}$) with the unitary transformation matrix $\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})$. Finally, the aggregate Hamiltonian matrix of Eq. (49) can be written in a form that emphasizes the separate contributions from atomic energies and atomic-pair interaction potentials,

$$\mathbf{H}_{\mathbf{S}}(\boldsymbol{R}) = 3E_{1s}\mathbf{I} + \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{V}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R}), \tag{51}$$

where the total interaction energy matrix is

$$\mathbf{V}(\boldsymbol{R}) = \begin{pmatrix} {}^3V_{ab} + V_{ac}^{(av)} + V_{bc}^{(av)} & V_{bc}^{(diff)} & V_{ac}^{(diff)} \\ V_{bc}^{(diff)} & {}^3V_{ac} + V_{ab}^{(av)} + V_{bc}^{(av)} & V_{ab}^{(diff)} \\ V_{ac}^{(diff)} & V_{ab}^{(diff)} & {}^3V_{bc} + V_{ab}^{(av)} + V_{ac}^{(av)} \end{pmatrix}. \tag{52}$$

Here, $V_{\alpha\beta}^{(av)} \equiv [{}^3V(R_{\alpha\beta}) + {}^1V(R_{\alpha\beta})]/2$ is the average and $V_{\alpha\beta}^{(diff)} \equiv [{}^3V(R_{\alpha\beta}) - {}^1V(R_{\alpha\beta})]/2$ one-half the difference of the triplet and singlet Heitler-London $H_2$ interaction energy curves, both of which vanish in the limit $R_{\alpha\beta} \to \infty$.

Carrying out the indicated matrix multiplications in Eq. (51) shows that $\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{13} = \{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{23} = 0$, as expected, and that $\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{12}$ is generally small, vanishing identically in high-symmetry atomic arrangements $[C_{2v},\, D_{\infty h},\, D_{3h}]$. In these cases, $\Theta(\boldsymbol{R}) \rightarrow 0$ and the diagonal Hamiltonian matrix elements of Eqs. (51) and (52) take the simple forms

$$\{\mathbf{H_S}(\boldsymbol{R})\}_{11} = 3E_{1s} + \frac{1}{4}\{3\,{}^1V_{ab} + {}^3V_{ab}\} + \frac{1}{4}\{3\,{}^1V_{ac} + {}^3V_{ac}\} + \{{}^1V_{bc} + {}^3V_{bc}\} \qquad (53a)$$

$$\{\mathbf{H_S}(\boldsymbol{R})\}_{22} = 3E_{1s} + \frac{1}{4}\{3\,{}^3V_{ab} + {}^1V_{ab}\} + \frac{1}{4}\{3\,{}^3V_{ac} + {}^1V_{ac}\} + \frac{1}{4}\{{}^3V_{bc} + 4\,{}^1V_{bc}\} \qquad (53b)$$

$$\{\mathbf{H_S}(\boldsymbol{R})\}_{33} = 3E_{1s} + \frac{5}{3}\{{}^3V_{ab} + {}^3V_{ac} + {}^3V_{bc}\}, \qquad (53c)$$

although more generally these elements depend explicitly on the $\Theta(\boldsymbol{R})$ value of Eq. (46b). The particular energy values given by Eqs. (53) are helpful in examining the limiting behaviors of the surfaces in high symmetry and prove useful in comparisons with related theoretical approaches made in the following Section 4.

A series of numerical evaluations of the foregoing expressions are performed in a 12-term Gaussian-orbital representation of the $1s$ atomic hydrogen orbital. This basis provides an orbital energy (-0.4999 *au*) in good agreement with the correct value, and a molecular hydrogen ground-state equilibrium interatomic separation ($R_e = 1.642\ a_0$) and total energy (-1.1157 *au*) in good agreement with the accepted Heitler-London values [17]. Conventional Gaussian-based computational methods are employed in evaluations of all information required in this particular implementation of the atomic-pair development for $H_3$ [5,6].

In Fig. 1 are shown contour plots of the two doublet eigenvalues of the $\mathbf{S}(\boldsymbol{R})$ matrix of Eqs. (44) and (45) for $H_3$ obtained in the Gaussian $1s^3$ representation for non-symmetric collinear atomic arrangements. The $\{\mathbf{S}_d(\boldsymbol{R})\}_1$ eigenvalue surface of Fig. 1(a) has a maximum near the saddle point ($R_s$= x.xx $a_0$) of the surface, decreases rapidly to zero in the united-atom limit $R_{ab} = R_{ac} \rightarrow 0$, approaches 1 in the three-body break-up limit $R_{ab} = R_{ac} \rightarrow \infty$, and goes to 2 in the diatomic limits $R_{ab} \rightarrow 0, R_{ac} \rightarrow \infty$ and $R_{ab} \rightarrow \infty, R_{ac} \rightarrow 0$. The vanishing of the eigenvalue of Fig. 1(a) as $R_{ab}$ and $R_{ac} \rightarrow 0$, corresponding to formation of a non-Pauli $1s^3$ atomic Li configuration, indicates that the minimal $1s^3$ basis does not support a physically significant $H_3$ state near the triatomic united-atom limit. The smaller doublet eigenvalue $\{\mathbf{S}_d(\boldsymbol{R})\}_2$ surface shown in Fig. 1(b) is evidently less structured than that of Fig. 1 (a) and vanishes in both the diatomic and triatomic united-atom limits, as does the quartet eigenvalue (not shown), which limits can be inferred from Eqs. (44) and (45). The S-matrix eigenvalue surfaces evidently identify atomic configurations in which improper states arise, provide information complementary to the associated energy surfaces, and can anticipate the presence of crossings in the corresponding potential-energy surfaces on basis of their degeneracies, as demonstrated in further detail below.

Figure 2 provides constant-energy contour plots of the matrix elements $\{\mathbf{H_S}(\boldsymbol{R})\}_{11}$ and $\{\mathbf{H_S}(\boldsymbol{R})\}_{22}$ obtained from Eqs. (51) and (52) for the non-symmetric collinear atomic arrangements of Fig. 1. These well-known energy surfaces are presented here to illustrate the extent of agreement obtained with corresponding conventional valence-bond calculations in a $1s^3$ basis, to demonstrate their general accordance with accurate quantum-chemistry calculations [32-35], and for comparison with the less familiar S-matrix eigensurfaces of Fig. 1. Specifically, the calculated saddle-point energy (-1.5735 *au*) of Fig. 2(a) compares well with that obtained from valence-bond calculations (-1.5834 *au*) in the same basis, placing the saddle point approximately 0.0735 *au* (2.00 eV) below the three-body (H+H+H) breakup energy of -1.500 *au* (-40.82 eV), and providing approximately 50% of the accepted accurate saddle-point binding energy of 0.1570 *au* (4.273 eV) relative to the three-body breakup limit at a geometry ($\mathrm{R}_s$ = x.xx $a_0$) in general accord with the accepted position ($R_s = 1.757\ a_0$) [32-35]. The calculated saddle-point energy relative to the two-body break-up energy (H + $H_2$) provides a (1.14x eV) barrier to the exchange reaction which is in accord with the valence-bond calculations (0.876x eV) but is approximately a factor of two to three times larger than the accepted value of 0.4166 eV [32-35], emphasizing the well-known sensitivity of this energy difference to the computational approximation employed.

The structure of the $H_3$ ground-state energy surface of Fig. 2(a) is evidently complementary to that of the associated S-matrix eigenvalue surface of Fig. 1(a), with the topography of the S-matrix eigensurface largely anti-correlated with that of the corresponding energy surface, the larger energies associated with smaller S-matrix eigenvalues. Similarly, the energy surface for the excited doublet state shown in Fig. 2(b) is seen to be monotonically increasing from the three-atom break-up limit as the diatomic and triatomic united-atom limits are approached, and consequently anti-correlated with the monotonically decreasing form of the associated S-matrix eigenvalue surface of Fig. 1(b). Of course, such behaviors can be expected more generally only for small basis set evaluations, or of the lower-lying S-matrix eigensurfaces, in view of the ultimate convergence of the highest-lying eigensurfaces to the redundancy factor $Q$ of Eq. (9) in a manner largely independent of atomic arrangement. The quartet-state energy surface is found to be repulsive with decreasing atomic separations for all non-symmetric collinear atomic arrangements, in accordance with the approximation of Eq. (53c), and is not depicted here.

In Fig. 3 are shown comparisons of the first two doublet energies in $H_3$ for symmetric collinear ($R_{ab} = R_{ac}$) atomic arrangements obtained from Eqs. (53a) and (53b) with corresponding valence-bond calculations. Evidently, the present results for the ground-state energy surface are in good agreement with the corresponding $1s^3$ valence-bond calculations which include only covalent structures ($\circ$), and are also in accord with valence-bond results which include all possible ionic configurations ($\bullet$) in the $1s^3$ basis. The first excited doublet state in $H_3$ is seen to be repulsive, in good agreement with the valence-bond calculations and in qualitative accord with previously reported accurate calculations, although this excited doublet is known to undergo an avoided crossing with a higher-lying state which is not included in the present development [34]. Although the results of Fig. 3 for the ground-state energy surface appear to bound the valence-bond results from above, this is only a happenstance in view of the small basis set employed. Indeed, similar apparent boundedness is not found for the excited doublet state in Fig. 3, although both results are clearly in satisfactory agreement with both forms of the valence-bond calculations, the ionic configurations making only small contributions to the ground-state surface but somewhat more significant contributions to the excited-state surface.

Figure 4 depicts contour plots of the two doublet S-matrix eigenvalues in $H_3$ of Eq. (45a) for $C_{2v}$ arrangements in which the $R_{ab} = R_{ac}$ separations are co-varied and the apex angle $\theta$ ranges from 30 to 180 degrees. A seam of intersection of these two surfaces is indicated by the cusps in the contours at $\theta = 60$ degrees, which corresponds to the familiar degeneracy associated with $D_{3h}$ symmetry. That is, comparisons of the surfaces in panels (a) and (b) of Fig. 4 shows the two surfaces to pass through one another, the former depicting the higher-value eigensurface to the right of the 60 degree line and the lower-value eigensurface to the left of this line of intersection. Correspondingly, panel (b) shows the reversed arrangement, with the lower eigenvalue surface to the right and the higher to the left of the 60 degree line. The associated more familiar energy surfaces for the ground- and first-excited $H_3$ states for $C_{2v}$ atomic arrangements obtained from Eqs. (53a) and (53b) shown in Fig. 5 similarly depict the expected $D_{3h}$ degeneracy and the associated surface crossing along the $\theta = 60$ degrees line formed by the cusps in the contours, in a manner complementary to the corresponding seam of intersection anticipated by the metric-matrix eigenvalues of Fig. 4.

In Fig. 6 are shown comparisons of the two doublet energies of Eqs. (53a) and (53b) with coresponding valence-bond calculations for the $C_{2v}$ atomic arrangements of Fig. 5 in which $R_{ab} = R_{ac} = 1.64\ a_0$ are held fixed and $\theta$ is varied from 20 to 180 degrees. Evidently, the present results for both surfaces are in good agreement with the corresponding $1s^3$ valence-bond calculations which include only covalent structures (○), and are also in accord with valence-bond results which include all possible ionic configurations (●) in the $1s^3$ basis. The crossing of the two surfaces when $\theta = 60$ degrees is evident in the figure, and in good agreement with the valence-bond calculations. As in Fig. 3, the apparent upper bound provided by the present results on the valence-bond calculations in the case of the ground-state surface in Fig. 6 is a happenstance in view of the small basis representation employed, with a similar apparent upper boundedness not present in the case of the excited doublet state.

Finally, Figs. 7 and 8 depict contours of constant S-matrix eigenvalues of Eq. (45a) and energies of Eqs. (53a) and (53b) for T-shaped $C_{2v}$ arrangements in $H_3$ in which both the width ($w$) and the height ($h$) of the T are varied. Evidently, both sets of these contours depict the seams of intersection along the line $w = 1.115\ h$ of $D_{3h}$ symmetry associated with the surface crossings as the degenerate configuration is reached, confirming that the intersection of the S-matrix surfaces again anticipates the corresponding crossing in the more familiar energy surfaces. As in Figs. 4 and 5, the two sets of eigenvalue surfaces in Figs. 7 and 8 depict the higher- and lower-valued portions of two smooth surfaces which intersect at the indicated seam. Quantitative comparisons of these results for fixed $w = 1.64$ $a_0$ as a function of $h$ with the valence-bond calculations shown in Fig. 9 confirms again the good agreement obtained between the present results and corresponding valence-bond calculations in this simple example.

## 4.0 Comparative and Concluding Remarks

The common features of previously devised semi-empirical approaches for incorporating fragment information in electronic structure calculations are indicated in Section 4.1, detailed analyses of the atom-in-molecules [13] and diatomics-in-molecules [14] methods in the context of the present development are reported in Sections 4.2 and 4.3, respectively, and concluding remarks in summary of the present report are provided in Section 4.4.

### 4.1 Fragment-Based Semi-Empirical Electronic Structure Approaches

The aims and objectives of the present *ab initio* development are closely related to those of earlier semi-empirical valence-bond-like attempts to incorporate atomic and diatomic information in studies of the electronic structures of molecules [13,14]. The development of the foregoing Sections 2 and 3 provides an analytical perspective from which to critically examine the theoretical foundations of these earlier methods.

The theoretical formulations of the particular semi-empirical methods of interest here are based on adoption of the ultimately singular Hamiltonian matrix

$$\mathbf{H}_A(\boldsymbol{R}) \equiv \langle \hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) | \hat{H}(\boldsymbol{r}:\boldsymbol{R}) | \hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) \rangle \tag{54}$$

constructed in a non-othogonal explicitly antisymmetric atomic spectral-product representation, and subsequent solution of the matrix Schrödinger equation [16]

$$\mathbf{H}_A(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{A}}(\boldsymbol{R}) = \mathbf{S}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{A}}(\boldsymbol{R}) \cdot \mathbf{E}(\boldsymbol{R}). \tag{55}$$

Commutation of the operators $\hat{P}_A$ and $\hat{H}(\boldsymbol{r}:\boldsymbol{R})$ in the Hamiltonian matrix of Eq. (54) gives

$$\mathbf{H}_{\mathbf{A}}(\boldsymbol{R}) = \langle \hat{P}_A \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) | \hat{P}_A | \hat{H}(\boldsymbol{r}:\boldsymbol{R}) \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) \rangle$$

$$= Q^{1/2}\langle \hat{P}_A \mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}(\boldsymbol{r}:\boldsymbol{R})\mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle, \tag{56}$$

with the atoms-in-molecules [13] and diatomics-in-molecules [14] approaches employing different approximations to the vector $\hat{H}(\boldsymbol{r}:\boldsymbol{R})\mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})$ in Eq. (56). The notational conventions of the present development are employed in Eqs. (54) to (56) in order to present the earlier developments in forms most convenient for comparative purposes.

### 4.2 Atoms-in-Molecules Method

The atoms-in-molecules method of Moffitt [13,36] has been the subject of early evaluations [37,38] and continuing but largely indecisive refinements [39-43]. In the original theoretical formulation [13], the aforementioned vector in Eq. (56) is given by the expression $\hat{H}(\boldsymbol{r}:\boldsymbol{R})\mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R}) = \mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})\cdot\mathbf{W} + \hat{V}(\boldsymbol{r}:\boldsymbol{R})\mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})$, where the matrix $\mathbf{W} \equiv \sum_{\alpha=1}^{N}\mathbf{H}^{(\alpha)}$ is the sum of atomic Hamiltonian matrices of Eq. (7) and the operator $\hat{V}(\boldsymbol{r}:\boldsymbol{R}) \equiv \sum_{\alpha=1}^{N}\sum_{\beta=N+1}^{N}\hat{V}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})$ is the sum of the atomic-pair interaction potentials of Eq. (5). This expression is an identity when the atomic spectral eigenstates employed are exact solutions of their respective atomic Schrödinger equations, in which case the associated Hamiltonian matrix of Eq. (56) becomes

$$\mathbf{H}_{\mathbf{A}}(\boldsymbol{R}) = \mathbf{S}(\boldsymbol{R})\cdot\mathbf{W} + Q^{1/2}\langle \hat{P}_A \mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{V}(\boldsymbol{r}:\boldsymbol{R})|\mathbf{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle. \tag{57}$$

In the absence of exact atomic eigenstates, a semi-empirical attitude is adopted in which Eq. (57) is used to provide an approximation to the Hamiltonian matrix of Eq. (54) by employing experimental atomic energies in the diagonal matrix $\mathbf{W}$ and suitable corresponding atomic eigenstates, introduced in an attempt to provide reliable estimates of the Coulombic interaction terms in Eq. (57) which would be obtained using the correct atomic eigenstates, were they available [13].

Although the ideas motivating the atoms-in-molecules approach have considerable merit, the development of Eqs. (54) to (57) is flawed in a number of fundamental aspects which have not been addressed in the attempted refinements reported to date [36-43]. Specifically, the two matrices on the right-hand side of Eq. (57) are generally not Hermitian, even in the case of use of exact atomic spectral eigenstates, so that neither have any physical significance. Moreover, *ad hoc* enforcement of individual Hermiticity of the two matrices results in a commonly employed Hermitian expression $(1/2)(\mathbf{S}(\boldsymbol{R})\cdot\mathbf{W}+\mathbf{W}^{\dagger}\cdot\mathbf{S}(\boldsymbol{R})^{\dagger})$ for the atomic terms which does not avoid the presence of the ultimately singular metric matrix. Accordingly, when the antisymmetric basis becomes linearly dependent, the solution of Eq. (55) becomes unstable. Although the consequences of this instability have been often noted, the generality and extent of the linear dependence of an antisymmetrized atomic spectral-product basis does not appear to have been fully appreciated in the literature. In Fig. 10 are shown as an example the eigenvalues of the metric matrix of Eq. (10) for $H_3$ molecules in symmetric collinear arrangements constructed in $2s1p$ and $3s2p$ Slater basis sets following the development of Section 3.3. Evidently, even in the smaller $2s1p$ basis set employed in panel (a) there are a significant number of eigenvalues near the lower limiting point of accumulation of the spectral interval approriate for $H_3$ (0 - 6), which clustering persists even at larger values of interatomic separation $R_{ab} = R_{ac}$. In the bigger $3s2p$ basis set of panel (b), the S-matrix eigenvalues are seen to become increasingly dense at the lower limiting point, in accordance with the clustering expected at the zero point of accumulation in the spectrum of a compact operator [25]. This common feature of compact operators can be expected to appear in the atomic spectral-product representations of aggregate electron permutation operators in cases of many-electron atoms quite generally.

It is clear that the metric matrices in both basis sets of Fig. 10 are highly singular, requiring elimination of the linearly-dependent basis states by adoption of canonical or other orthogonalization procedures. Attempts to isolate the non-singular portion of the Hamiltonian matrix of Eq. (57) in this way, however, result in an unfortunate sensitivity to the atomic energies employed in the $\mathbf{W}$ matrix appearing there [39-43]. Additionally, use of the aforementioned Hermitian form of the atomic terms in Eq. (57) generally renders largely invalid attempts to isolate the linearly-independent subspace of the antisymmetric aggregate basis by unitary transformation [43], suggesting that only the smallest possible basis sets can be reliably employed in the atoms-in-molecules development of Eqs. (54) to (57) in the absence of modification.

A more fundamental difficulty associated with the Hamiltonian of Eqs. (56) than that indicated in the foregoing is revealed in the course of attempts to intepret the Moffitt development of Eqs. (54) to (57) as a computationally viable approach in which the spectral-product Hilbert space $\mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R})$ potentially has a limit of completion. Writing the vector in Eq. (56) in this case in the form $\hat{H}(\boldsymbol{r} : \boldsymbol{R})\mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \rightarrow \mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R})$, which expression is exact in the closure limit, gives $\mathbf{H_A}(\boldsymbol{R}) \rightarrow \mathbf{S}(\boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R})$, where $\mathbf{H}(\boldsymbol{R})$ is the spectral-product Hamiltonian matrix of Eq. (7). In this case, Eq. (55) becomes

$$\mathbf{S}(\boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U_A}(\boldsymbol{R}) = \mathbf{S}(\boldsymbol{R}) \cdot \mathbf{U_A}(\boldsymbol{R}) \cdot \mathbf{E}(\boldsymbol{R}), \tag{58}$$

from which the metric matrix $\mathbf{S}(\boldsymbol{R})$ might be factored were it not for the fact that it is generally singular and, consequently, does not have an inverse.

Since the matrices $\mathbf{S}(\boldsymbol{R})$ and $\mathbf{H}(\boldsymbol{R})$ in Eq. (58) generally fail to commute in any finite representation, the Hamiltonian $\mathbf{S}(\boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R})$ appearing there is not Hermitian, in spite of the fact that $\mathbf{H_A}(\boldsymbol{R})$ of Eq. (56) is Hermitian and the operators $\hat{P}_A$ and $\hat{H}(\boldsymbol{r} : \boldsymbol{R})$ commute. That is, the atomic spectral-product basis does not provide a faithful representation of the commuting operators $\hat{P}_A$ and $\hat{H}(\boldsymbol{r} : \boldsymbol{R})$ in the form of the matrices $\mathbf{S}(\boldsymbol{R})$ and $\mathbf{H}(\boldsymbol{R})$, rendering the development of Eqs. (54) to (58) invalid in any finite representation. This failure follows from the fact that the operation $\hat{P}_A\mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R})$ is not closed in any finite Hilbert space $\mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R})$ of Eq. (3). In the closure limit, however, $\hat{P}_A\mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \rightarrow Q^{-1/2}\mathbf{\Phi}(\boldsymbol{r} : \boldsymbol{R}) \cdot \mathbf{S}(\boldsymbol{R})$, and a unitary transformation $\mathbf{U}(\boldsymbol{R})$ can be found which simultaneously diagonalizes both the Hamiltonian matrix $\mathbf{H}(\boldsymbol{R})$ of Eq. (7) and the metric matrix $\mathbf{S}(\boldsymbol{R})$ of Eq. (10), in accordance with the commutation of the two associated operators. In this event, the matrices $\mathbf{S}(\boldsymbol{R}) = \mathbf{U}(\boldsymbol{R}) \cdot \mathbf{S}_d(\boldsymbol{R}) \cdot \mathbf{U}(\boldsymbol{R})^\dagger$ and $\mathbf{H}(\boldsymbol{R}) = \mathbf{U}(\boldsymbol{R}) \cdot \mathbf{E}(\boldsymbol{R}) \cdot \mathbf{U}(\boldsymbol{R})^\dagger$ commute, with the spectrum of $\mathbf{S}_d(\boldsymbol{R})$ comprising the lower and upper end point vaules 0 and $Q$ of Eq. (9) in this limit.

In spite of the aforementioned complications, the non-singular portion of the Hamiltonian matrix appearing in Eq. (58) can be extracted in finite representations, as well as in the limit of closure, following the development of Section 2.0. Specifically, isolating the physical block of the Hamiltonian matrix of Eq. (56) in accordance with Eq. (8) and setting $\mathbf{H_A}(\boldsymbol{R}) \rightarrow \mathbf{S}(\boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R})$ there gives

$$\{\mathbf{H_S}(\boldsymbol{R})\}_{pp} \equiv \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2} \cdot \{\mathbf{U_S}(\boldsymbol{R})^\dagger \cdot \mathbf{H_A}(\boldsymbol{R}) \cdot \mathbf{U_S}(\boldsymbol{R})\}_{pp} \cdot \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2}$$

$$= \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2} \cdot \{\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^\dagger \cdot \mathbf{S}(\boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} \cdot \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2}$$

$$= \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{+1/2} \cdot \{\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^\dagger \cdot \mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} \cdot \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2}$$

$$\to \{\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^\dagger \cdot \mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_{pp}. \qquad (59)$$

Equation (59) is seen to constitute a similarity transformation of the Hamiltonian matrix of Eq. (8) in finite orders which converges to the physical block of the spectral-product Hamiltonian matrix of Eq. (8) in the closure limit, evidently resulting in a computational approach essentially identical with that of Eqs. (1) to (12). Accordingly, it is seen that a strictly Hermitian matrix representation suitable for computational applications is obtained from Moffitt's development when its non-singular terms are isolated employing Eq. (59), in which event a closure limit can be properly attained in accordance with the spectral theory of Sections 2 and 3, and the distinction between use of explicitly antisymmetric and spectral-product basis states becomes inconsequential.

### 4.3 Diatomic-in-Molecules Method

The diatomics-in-molecules approach has been the object of continuing applications and refinements through the years [44-56]. In the most commonly employed realizations of the original development of Ellison [14], the vector in Eq. (56) is written [46-50]

$$\hat{H}(\boldsymbol{r}:\boldsymbol{R})\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) = \sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) - \frac{(N-2)}{(N-1)}\big(\hat{H}^{(\alpha)}(\boldsymbol{i}) + \hat{H}^{(\beta)}(\boldsymbol{j})\big)\Big\}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}), \qquad (60)$$

employing Eq. (13) and the notation of the present development. In this case, Eq. (56) becomes

$$\mathbf{H}_A(\boldsymbol{R}) = Q^{1/2}\sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\langle\hat{P}_A\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle$$

$$-\frac{(N-2)}{(N-1)}\langle\hat{P}_A\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}^{(\alpha}(\boldsymbol{i}) + \hat{H}^{(\beta}(\boldsymbol{j})|\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle\Big\}$$

$$= \mathbf{S}(\boldsymbol{R})\cdot\sum_{\alpha=1}^{N}\sum_{\beta=\alpha+1}^{N}\Big\{\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}\cdot\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) - \frac{(N-2)}{(N-1)}\big(\mathbf{H}^{(\alpha)} + \mathbf{H}^{(\beta)}\big)\Big\}, \qquad (61)$$

where $\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \equiv \langle \hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle = (Q^{(\alpha,\beta)})^{1/2}$ $\langle \hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle$ is the diatomic Hamiltonian matrix in the non-orthogonal antisymmetrized spectral product pair basis $\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})$. The atomic integrals in the first line of Eq. (61) have been evaluated by employing the expression $\big(\hat{H}^{(\alpha)}(\boldsymbol{i}) + \hat{H}^{(\beta)}(\boldsymbol{j})\big)\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) = \boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\cdot\big(\mathbf{H}^{(\alpha)} + \mathbf{H}^{(\beta)}\big)$, whereas the diatomic integrals are evaluated in the form

$$
\begin{aligned}
&Q^{1/2}\langle \hat{P}_A\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle \\
&= Q^{1/2}(Q^{(\alpha,\beta)})^{-1/2}\langle \hat{P}_A\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})|\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle \\
&= Q^{1/2}(Q^{(\alpha,\beta)})^{-1/2}\langle \hat{P}_A\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})|\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\rangle\cdot\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}\cdot\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \\
&= \mathbf{S}(\boldsymbol{R})\cdot\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}\cdot\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \qquad (62)
\end{aligned}
$$

using the representation of $\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})$ in the basis $\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})$ in the form $\hat{H}^{(\alpha,\beta)}(\boldsymbol{i},\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})\hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) = \hat{P}_A^{(\alpha,\beta)}\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R})\cdot\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}\cdot\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$. The Schrödinger equation for the diatomic Hamiltonian matrix $\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$,

$$
\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\cdot\mathbf{U}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\cdot\mathbf{U}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\cdot\mathbf{E}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}), \qquad (63)
$$

can be used to formally eliminate the matrix $\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}$ in Eq. (62) by writing $\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}\cdot\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{U}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\cdot\mathbf{E}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\cdot\mathbf{U}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}$, in which form Eq. (62) is commonly employed [46-50]. The matrices $\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ and $\mathbf{E}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ of Eqs. (61) to (63) depend explicitly on both the magnitude and direction of the separation vector $\boldsymbol{R}_{\alpha\beta}$, as do the matrices $\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ and $\mathbf{U}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ of Eq. (63), in contrast to their counterparts of Eqs. (24) and (26), which are defined in terms of the rotated representations of Eq. (19).

The development of Eqs. (60) to (63) entails commutation of both aggregate and diatomic Hamiltonian operators with the corresponding antisymmetrizers, resulting in the appearance of both aggregate and diatomic metric matrices and the non-Hermitian forms of the atomic and diatomics Hamiltonian matrices in Eq. (61), the latter consequent of the failure of the metric and Hamiltonian matrices to commute in any finite representation.

Accordingly, instabilities associated with the linear dependencies arising from the aggregate and diatomic metric matrices can be expected to appear in applications based on the non-Hermitian diatomics-in-molecules expression of Eq. (61). Specifically, a sensitivity to input atomic and diatomic information indicated in connection with Eqs. (57) and (58) above also applies to the diatomics-in-molecules Hamiltonian matrix of Eqs. (60) to (63). Attempts to deal with the consequences of these circumstances include the widespread avoidance of the aggregate metric matrix by the *ad hoc* approximation $\mathbf{S}(\boldsymbol{R}) \rightarrow \mathbf{I}$, adoption of explicitly Hermitized forms of the atomic and interaction matrices, and dealing directly with the consequences of a non-Hermitian Hamiltonian formalism. Although many of the applications of Eq. (61) have shown considerable inventiveness in overcoming computational obstacles [44-56], the inherently flawed nature of the development has apparently precluded widespread adoption of the approach.

As in the case of the development of Section 4.2, a computationally viable diatomics-in-molecules approach can be based on the linearly-independent subspaces of explicity antisymmetric aggregate and diatomic spectral-product representations of Eqs. (40) and (41). Specifically, the non-singular block of Eq. (61) is isolated in the form [cf., Eq. (59)]

$$\begin{aligned}\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} &\equiv \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2} \cdot \{\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{H}_{\mathbf{A}}(\boldsymbol{R}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} \cdot \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2} \\ &= \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{+1/2} \cdot \sum_{\alpha=1}^{N} \sum_{\beta=\alpha+1}^{N} \big\{\mathbf{U}_{\mathbf{S}}(\boldsymbol{R})^{\dagger} \cdot \mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1} \cdot \mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R}) \\ &\qquad - \frac{(N-2)}{(N-1)}\big(\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R})\big)\big\}_{pp} \cdot \{\mathbf{S}_d(\boldsymbol{R})\}_{pp}^{-1/2}, \qquad (64)\end{aligned}$$

where $\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R})$ and $\mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R})$ are the transformed atomic-energy matrices of Eq. (8) and the subscript "*pp*" on the diatomic terms refers to both the aggregate and diatomic representations. The latter terms in Eq. (64) can be evaluated by inserting the identities $\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} = \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{I}$ before after $\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}$, respectively, and noting that

$$\mathbf{S}_d^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1} = \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1} \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \qquad (65)$$

when restricted to the indicated linearly-independent diatomic subspace, to obtain

$$\mathbf{S}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1} \cdot \mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{S}_d^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1} \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$$

$$= \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{S}_{d}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1} \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger}$$

$$= \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \{\mathbf{S}_{d}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp}^{-1/2} \cdot \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp} \cdot \{\mathbf{S}_{d}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp}^{1/2} \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger}. \tag{66}$$

Here,

$$\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp} \equiv$$

$$\{\mathbf{S}_{d}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp}^{-1/2} \cdot \{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp} \cdot \{\mathbf{S}_{d}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp}^{-1/2} \tag{67}$$

is the linearly-independent block of the Hamiltonian matrix $\mathbf{H}_{\mathbf{A}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$, and only the non-singular portion of the diagonal matrix $\mathbf{S}_{d}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{-1}$ has been retained in the last line of Eq. (66) in accordance with the specification of Eq. (64). Finally, employing Eq. (66) in Eq. (64) and taking the closure limit as in Eqs. (40) to (42) gives

$$\{\mathbf{H}_{\mathbf{S}}(\boldsymbol{R})\}_{pp} = \sum_{\alpha=1}^{N} \sum_{\beta=\alpha+1}^{N} \left\{ \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} - \frac{(N-2)}{(N-1)} \{\mathbf{H}_{\mathbf{S}}^{(\alpha)}(\boldsymbol{R}) + \mathbf{H}_{\mathbf{S}}^{(\beta)}(\boldsymbol{R})\}_{pp} \right\} \tag{68}$$

for the diatomics-in-molecules Hamiltonian matrix, where

$$\{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} \equiv \{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp}^{\dagger} \cdot \{\mathbf{H}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{pp} \cdot \{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} \tag{69}$$

and

$$\{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R})\}_{pp} \equiv \{\mathbf{U}_{\mathbf{S}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{U}_{\mathbf{S}}(\boldsymbol{R})\}_{pp}. \tag{70}$$

Equations (68), (69), and (70) are seen to be identical with Eqs. (32), (33), and (42), respectively, when note is taken of the fact that the spatial frame transformation of Eqs. (19) to (21) has not been incorporated in the devlopment of Eqs. (64) to (70). When this transformation is introduced, the modified diatomics-in-molecules Hamiltonian of Eqs. (68) to (70) is seen to be identical with that obtained from the computational implementation of the spectral-theory in Section 3 employing explicitly antisymmetric basis states. Accordingly, a strictly Hermitian diatomic-in-molecules formalism suitable for computational applications is obtained from the original largely semi-empirical development when the insights provided by the spectral-theory of Sections 2 and 3 are incorporated into the analysis.

### 4.4 Concluding Remarks

The theoretical development reported here, in which antisymmetry requirements are applied subsequent to construction of the many-electron Hamiltonian matrix in an orthogonal spectral-product basis, provides an alternative perspective on electronic structure calculations of atoms, molecules, and other forms of matter. Permutation-symmetry basis states are seen to play a central role in the development, emphasizing the importance of the eigenspectrum of the matrix representatative of the aggregate electron antisymmetrizer, which is seen to converge to the two-point spectrum commonly associated with a compact operator. The approach provides for the definition of Hermitian matrix representatives of atomic and diatomic operators which individually have appropriate asymptotic separation limits, and which accommodate the incorporation of diatomic fragment information in forms free of *ad hoc* assumptions or approximations. The spectrum of the aggregate Hamiltonian matrix obtained in this way satisfies the Hylleraas-Undheim theorem for fixed dimensions of the permutation-symmetry-blocked diatomic Hamiltonian matrices as the dimensions of the aggregate permutation-symmetry basis is enlarged in a linear variational development. Accordingly, convergence to specific portions of the correct Hamiltonian eigenspectrum can be anticipated from the development employing converged representations of the underlying bare diatomic states constructed in sufficiently large spectral-product representations.

A particular computational implementation of the general development makes use of largely conventional methods of calculations for atoms and diatomic molecules, and can take advantage of the currently available highly developed methods devised for this purpose. The simple $H_3$ example studied illustrates the important role of the eigensurfaces of the metric matrix in identifying non-Pauli states in the aggregate spectral-product basis, on the one hand, and of the presence of linear dependence in the corresponding antisymmetrized basis, on the other. Additionally, the S-matrix eigensurfaces anticipate the general topological features of the corresponding more familiar potential energy surfaces, and, in particular, in case of the low-lying doublet states of $H_3$ are seen to anticipate the presence of well-known electronic-energy surface crossings at high-symmetry configurations. Additional calculations on other molecules which include many-electron atoms are required to confirm the promise of these illustrative applications to the $H_3$ molecule.

The development further provides a theoretical basis from which to analyze previously reported highly promising but largely unrealized methods for incorporating fragment information in electronic structure determinations [13,14]. The failure to obtain strictly faithful matrix representatives of the aggregate electron antisymmetrizer and Hamiltonian in the spectral-product basis, consequent of the absence of closure in the operation of the antisymmetrizer in any finite spectra-product representation, is seen to be the root cause of limitations and aberrant behaviors observed in applications of these approaches [44-50]. Specifically, the failure of the matrix representatives of the antisymmetrizer and Hamiltonian operators in the specral-product basis to faithfully represent the commutation of the defining operators leads to the appearance of non-Hermitian matrix representatives and instabilities associated with the singular nature of both aggregate and diatomic metric matrices. These limiting attributes of the earlier developments are overcome employing the more complete understanding of the role of the metric matrices provided by the spectral-theory analysis. Extraction of the non-singular portions of aggregate Hamiltonian matrices constructed in linearly-dependent, explicitly antisymmetrized basis sets are seen to result in commutationally viable expressions from both atoms-in-molecules and diatomics-in-molecules approaches which are identical with the results obtained here, providing confidence in applications of the modified versions of these earlier methods and of the present development.

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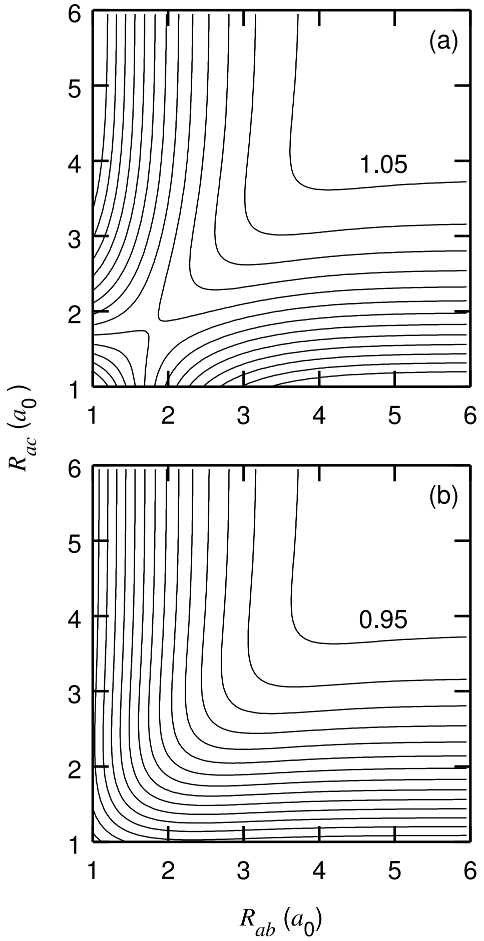

Figure 1–Constant-value contours for the two doublet eigenvalues (a) $\{\mathbf{S}_d(\boldsymbol{R})\}_1$ and (b) $\{\mathbf{S}_d(\boldsymbol{R})\}_2$ of the $\mathbf{S}(\boldsymbol{R})$ matrix of Eqs. (44) and (45) for collinear atomic configurations of $H_3$. The coordinate axes give the distances $R_{ab}$ and $R_{ac}$ between the central atom located at the origin and the outer atoms, measured in atomic units ($a_0$), employing an increment/decrement of 0.1 between adjacent contours. In panel (a) the contours increase uniformly in value from that labeled 1.05, except as $R_{ab} = R_{ac} \to 0$ inside the saddle point, in which region the values decrease monotonically to zero, whereas in panel (b) the contour values decease uniformly from that labeled 0.95, as is discussed further in the text.

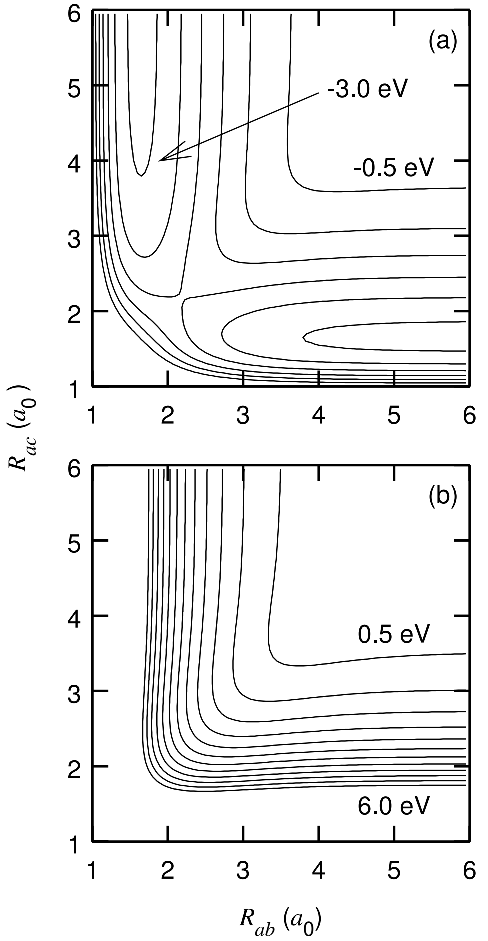

Figure 2–Constant-energy contours for the ground (a) and first-excited (b) doublet-state potential energy surfaces of $H_3$ for non-symmetric collinear atomic arrangements, obtained from the matrix elements $\{\mathbf{H_S}(\boldsymbol{R})\}_{11}$ and $\{\mathbf{H_S}(\boldsymbol{R})\}_{22}$ of Eqs. (51) and (52). The coordinate axes are as in Fig. 1, measured in atomic units ($a_0$), the zero of energy employed (-1.50 $au$) is that of the three-atom dissociation limit (H+H+H), and an energy decrement/increment of 0.5 eV is employed between contours. Panel (a) depicts the familiar saddle and diatomic structures of the ground-state energy surface in $H_3$, whereas the excited-state energy surface of panel (b) is montonically increasing with decreasing separations $R_{ab}$ and/or $R_{ac}$, as is discussed further in the text.

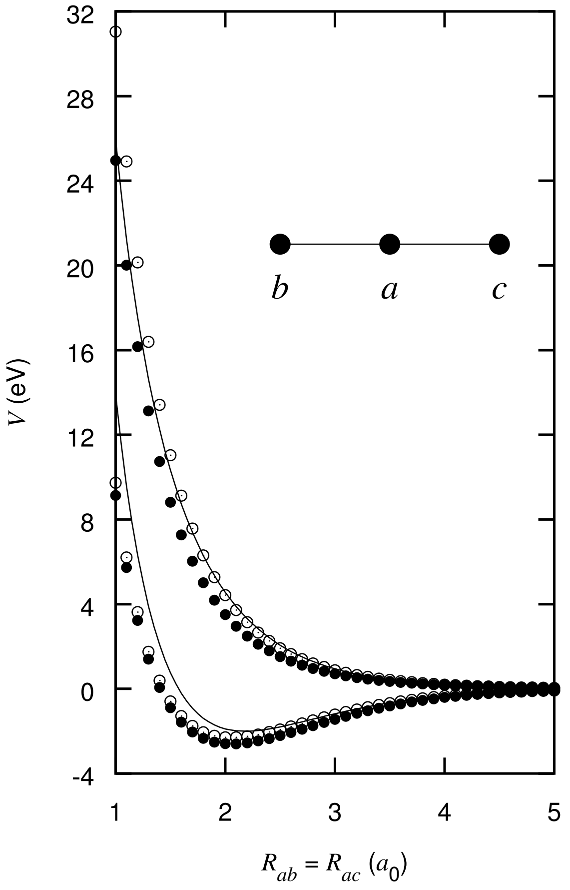

Figure 3–Ground and first-excited doublet state energies in $H_3$ for symmetric collinear atomic arrangements. The solid curves depict the values obtained from Eqs. (53a) and (53b), respectively, of the present development, whereas the data points are obtained from conventional valence-bond calculations in a $1s^3$ basis set including (•) and excluding (○) ionic configurations. The zero of energy (-1.50 *au*) is that of the three-atom dissociation limit (H+H+H), as in Fig. 2.

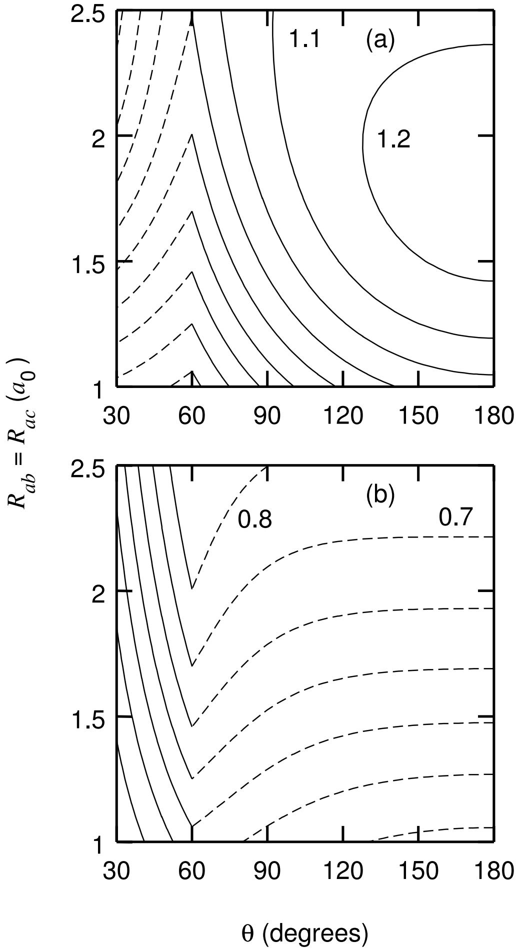

Figure 4–Constant-value contours for the two doublet eigenvalues (a) $\{\mathbf{S}_d(\boldsymbol{R})\}_1$ and (b) $\{\mathbf{S}_d(\boldsymbol{R})\}_2$ of the $\mathbf{S}(\boldsymbol{R})$ matrix of Eqs. (44) and (45) for $C_{2v}$ atomic arrangements ($R_{ab} = R_{ac}$), where $\theta$ is the apex angle of the triatomic $H_3$ configuration, employing an increment/decrement of 0.1 between adjacent contours. The cusps in the contours of both panels indicate the presence of a seam of intersection in the two surfaces at the $\theta = 60$ degree line, with the contour values decreasing uniformly from right to left in panel (a) and decreasing uniformly from top to bottom in panel (b), as is discussed further in the text.

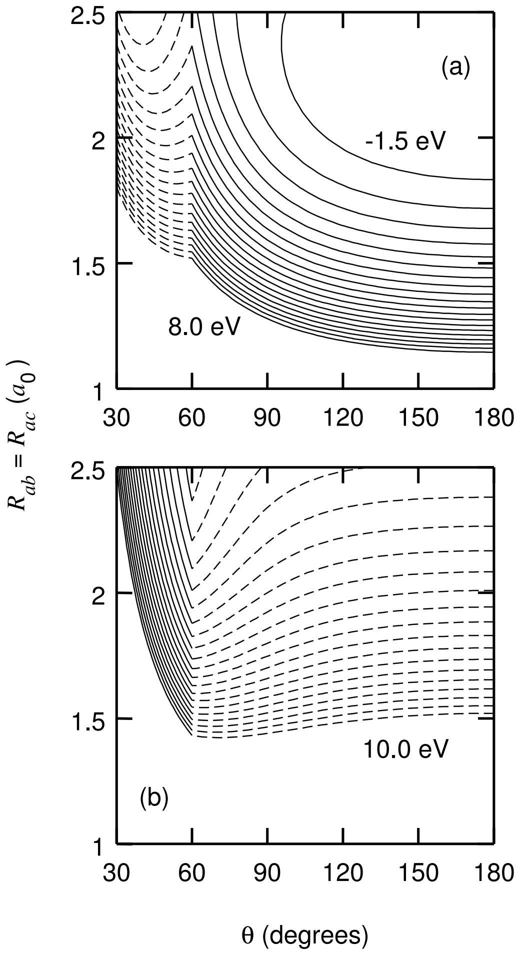

Figure 5–Constant-energy contours for the two lowest-lying doublet states of $H_3$ for $C_{2v}$ atomic arrangements ($R_{ab} = R_{ac}$), obtained from Eqs. (53a) and (53b), where $\theta$ is the apex angle of the triatomic configuration, employing an energy increment/decrement of 0.5 eV between adjacent contours. The zero of energy (-1.50 *au*) is that of the three-atom dissociation limit (H+H+H). The cusps in the contours of both panels indicate the familiar seam of intersection in the two energy surfaces at the $\theta = 60$ degree line in $D_{3h}$ symmetry, with the contour energy values increasing uniformly from top to bottom in both panels. Panel (a) depicts the lowest-lying surface only for large values of $\theta$, whereas panel (b) depicts the lowest-lying surface only for small $\theta$, as is discussed further in the text.

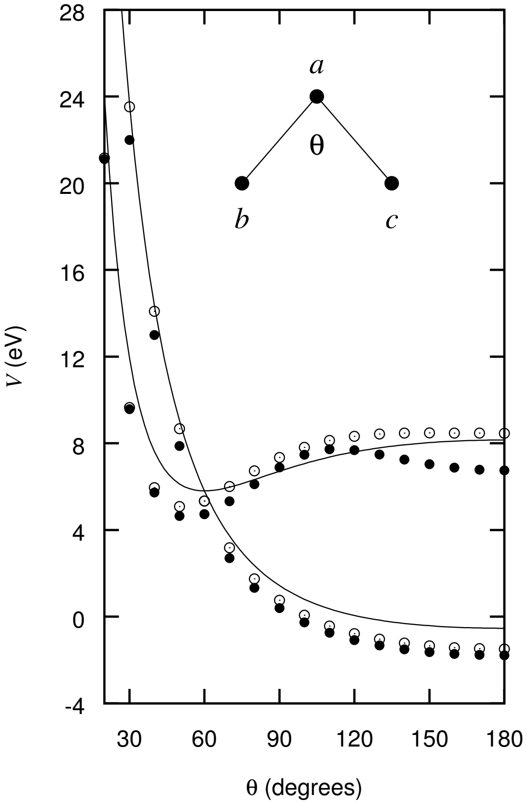

Figure 6–Ground and first-excited doublet-state energies in $H_3$ for $C_{2v}$ atomic arrangements ($R_{ab} = R_{ac} = 1.64\ a_0$), where $\theta$ is the apex angle of the triatomic configuration. The solid curves depict the values obtained from Eqs. (53a) and (53b) of the present development, whereas the data points are obtained from conventional valence-bond calculations in a $1s^3$ basis set including (●) and excluding (○) ionic configurations. The zero of energy (-1.50 $au$) is that of the three-atom dissociation limit (H+H+H), as in Fig. 5. The crossing point of the two curves corresponds to $D_{3h}$ symmetry, as discussed in the text.

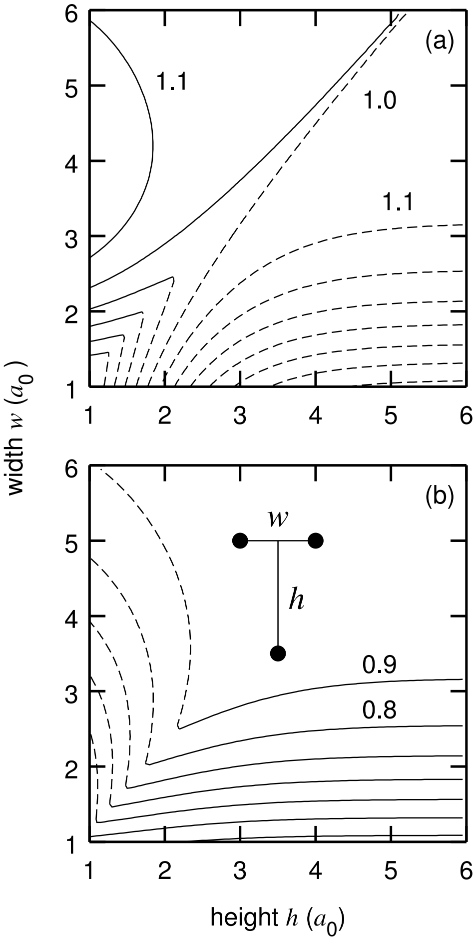

Figure 7–Constant-value contours for the two doublet eigenvalues (a) $\{\mathbf{S}_d(\boldsymbol{R})\}_1$ and (b) $\{\mathbf{S}_d(\boldsymbol{R})\}_2$ of the $\mathbf{S}(\boldsymbol{R})$ matrix of Eq. (44) and (45) for T-shaped atomic arrangements (width - $w$, height - $h$) in $H_3$, employing an increment/decrement of 0.1 between adjacent contours. In panel (a) the contours are monotonically increasing from that labelled 1.0, whereas in panel (b) they are monotonically increasing from that labelled 0.9. The cusps in the contours of both panels indicate the presence of a seam of intersection in the two surfaces along the $w = 1.155\ h$ line corresponding of $D_{3h}$ symmetry, as is discussed further in the text.

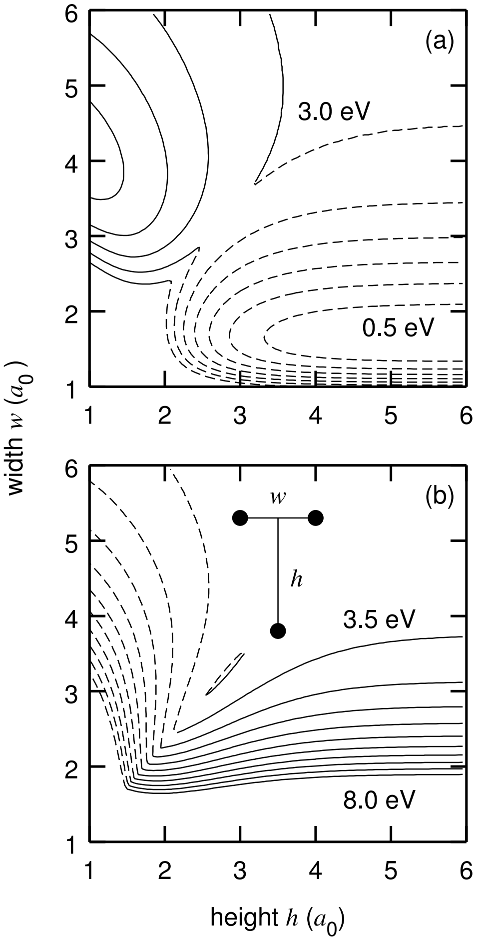

Figure 8–Constant-energy contours for the two lowest-lying doublet states of $H_3$ obtained from Eqs. (53a) and (53b) for T-shaped atomic arrangements (width - $w$, height - $h$), employing an energy increment/decrement of 0.5 eV between adjacent contours, with the zero of energy (-1.50 $au$) employed that of the three-atom dissociation limit (H+H+H). The cusps in the contours of both panels indicate the presence of a seam of intersection in the two surfaces along the $w = 1.155\ h$ line corresponding to $D_{3h}$ symmetry. Panel (a) depicts the lowest-lying surface only for large values of height $h$, whereas panel (b) depicts the lowest-lying surface only for small $h$, as is discussed further in the text.

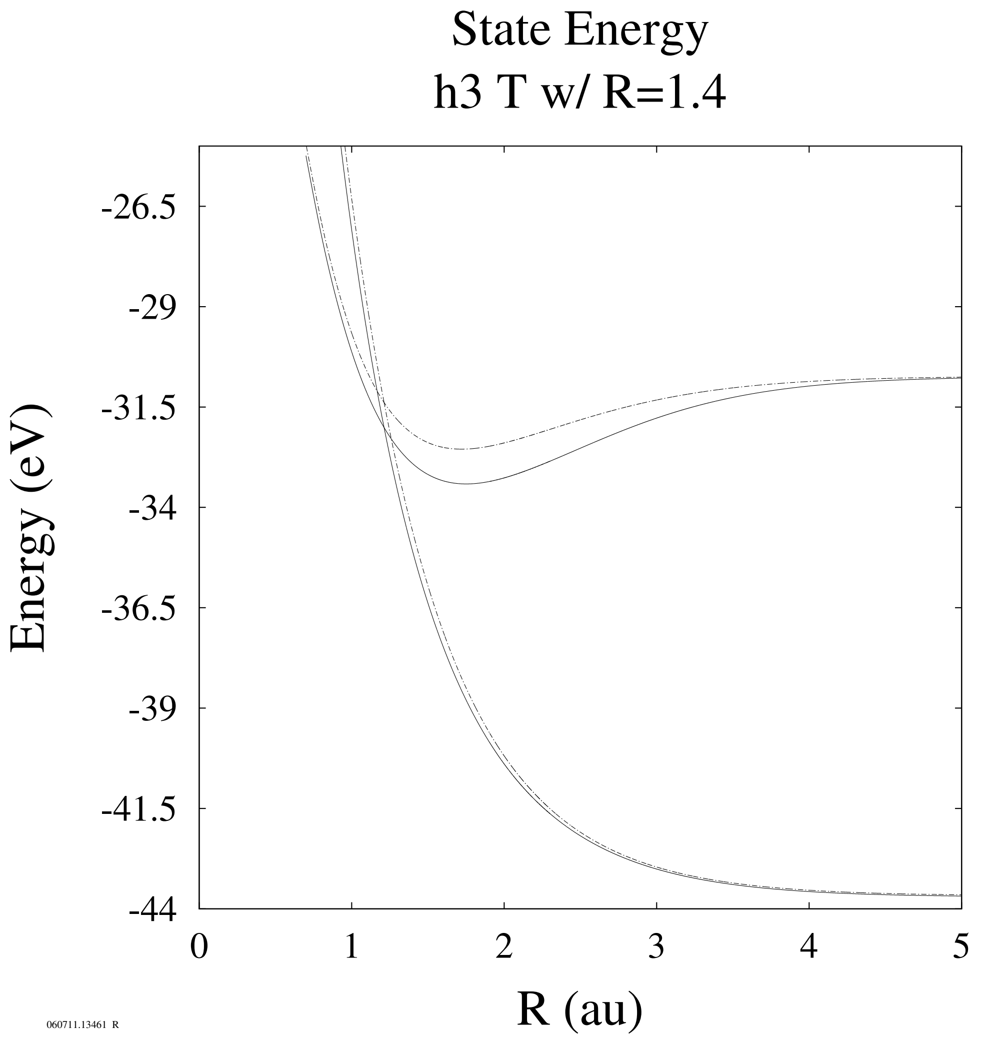

Figure 9–Ground and first-excited doublet-state energies in $H_3$ for T-shaped $C_{2v}$ atomic arrangements (width - $w = 1.64\ a_0$, height - $h$). The solid curves depict the values obtained from Eqs. (53a) and (53b) of the present development, whereas the data points are obtained from conventional valence-bond calculations in a $1s^3$ basis set including (●) and excluding (○) ionic configurations. The zero of energy (-1.50 $au$) is that of the three-atom dissociation limit (H+H+H), as in Fig. 8.

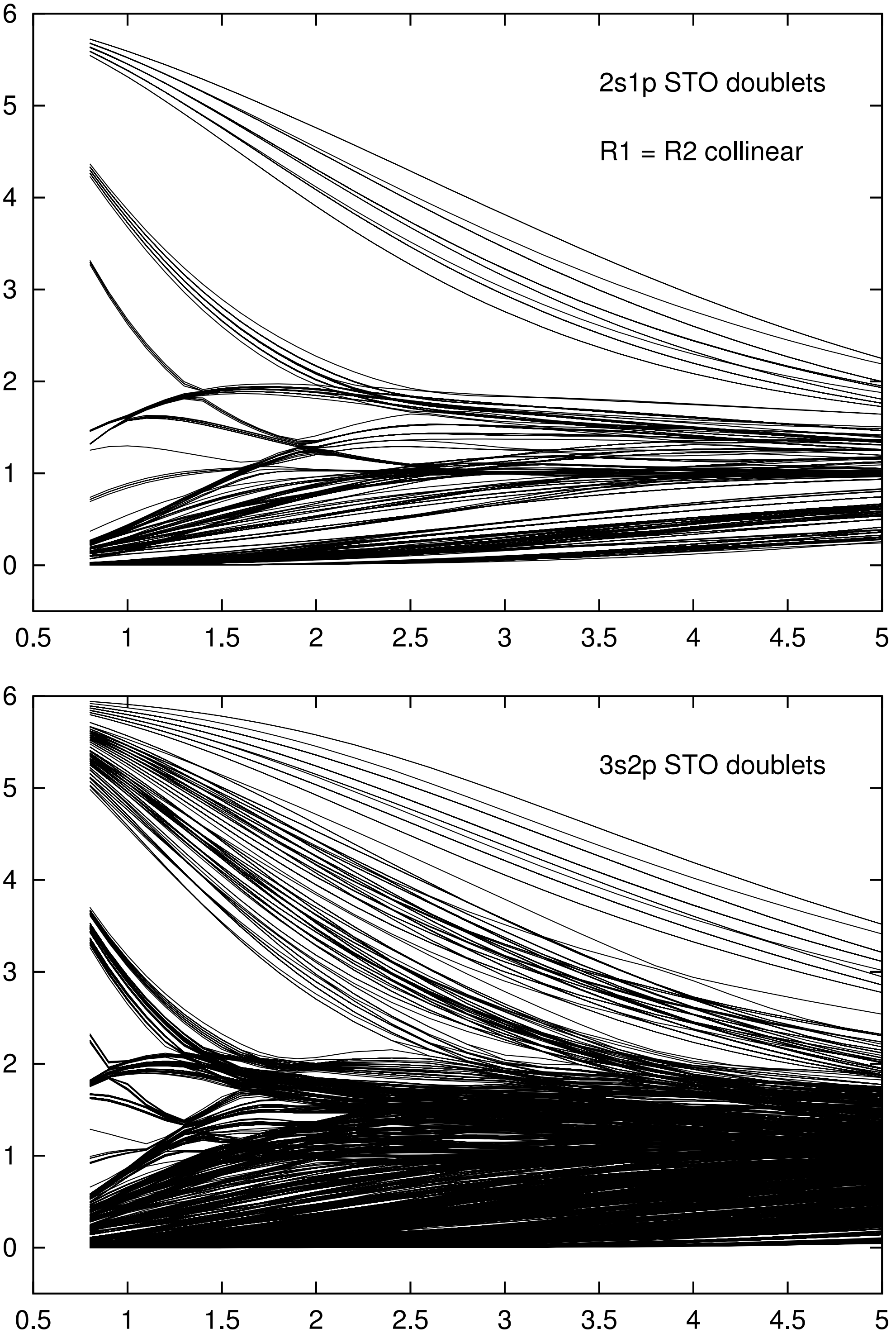

Figure 10–Eigenvalue spectra of the S-matrix for symmetric collinear $H_3$ constructed in (a) $2s1p$ and (b) $3s2p$ basis sets. The limiting points of the spectra are seen to be zero and $Q = n_t!/(n_1!n_2!n_3!) = 6$, with the latter eigenvalues corresponding to the totally antisymmetric states and the former to the unphysical (non-Pauli) states of Eqs. (9) to (11). The lower end of the spectrum corresponds to a point of accumulation, as discussed in the text.