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Spectral Theory of Chemical Bonding[†]

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Introduction

Adiabatic electronic wave functions (*1*) have long provided a useful starting point for quantitative predictions of chemical structures and the pathways of chemical reactions (*2*). Computational methods for such purposes commonly employ totally antisymmetric basis functions in repeated calculations of the total electronic energy of a molecule or other chemical aggregate at a large number of atomic configurations, with binding energies at stable structures obtained in this way by subtracting the calculated energies of the non-interacting constituent atoms. A similar approach is adopted in density-functional methods (*3*), which cleverly circumvent determinations of correlated many-electron wavefunctions but nevertheless calculate total energies, rather than binding energies, over the relevant range of aggregate geometries. Such methods have provided a great wealth of information on structures and selected physical properties of molecules, but they are arguably only computational prescriptions, rather than a quantum theory of chemical bonding in which interaction energies are expressed in terms of intrinsic atomic properties which can be determined once and for all (*4*).

Role of the Symmetric Group

A significant barrier to development of an atomic-interaction-based theory of chemical bonding is found in the antisymmetry requirement placed on physically admissible solutions of the Schrödinger equation (*5*). Specifically, the permutation symmetry group of a collection of N non-interacting atoms is given by the direct product group $S_{n_1} \otimes S_{n_2} \otimes \cdots S_{n_N}$ of the electron permutation groups $S_{n_1}, S_{n_2}, \cdots S_{n_N}$ of the individual atoms, which is a *subgroup* of the permutation group $S_{n_{total}}$ ($n_{total} = n_1 + n_2 + \cdots + n_N$) for the entire aggregate (*6*). As a consequence, the outer product of atomic eigenstates familiar from the perturbation theory of long-range interactions (*7*), which is correct in the atomic separation limit and provides an appropriately universal basis for describing chemical interactions (*8,9*), is reducible in $S_{n_{total}}$ and generally contains irreducible representations of $S_{n_{total}}$ other than the desired totally antisymmetric representation (*6,10*). Moreover, some of these non-totally-antisymmetric representations are known to contain unphysical continua in which the physical Schrödinger eigenstates can be embedded (*11,12*). Outer-product reduction methods for isolating the totally antisymmetric subspace of the atomic spectral-product basis (*6*) are not generally suitable for this construction (*10*), and symmetry-adapted perturbative approaches which adopt alternative strategies to accomplish the required isolation of the totally antisymmetric subspace are either ineffectual or are inappropriate for the large charge distortions consequent of chemical bonding (*12,13*). Of course, the usual prior antisymmetrization of

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the basis does not allow the desired separation of the Hamiltonian matrix into constituent atomic energies and their interactions in the aggregate, and can give rise to linear dependence and related computational instabilities. New approaches which can overcome the difficulties associated with employing an atomic-product representation in studies of chemical interactions, while retaining the conceptual and computational advantages of such an interaction-energy-based approach, are clearly required.

Spectral Theory

In the present report, a new theoretical approach to chemical bonding is described based on the outer spectral-product representation of the interacting atoms (7-9). The aforementioned symmetric-group issues are overcome by deferring enforcement of wave function antisymmetry until *after* the construction of the matrix representative of the Hamiltonian in the spectral-product basis. The aggregate Hamiltonian matrix obtained in this way is additive in the energies of the atomic constituents and in their pairwise interactions. The atomic interaction-energy matrices can be expressed entirely in terms of spectral representatives of the electronic number-density operators of the individual atoms, which provide the computational invariants of the formalism. Since the required atomic spectral information can be determined once and for all from conventional electronic structure calculations, there is no need for the repeated evaluations of Hamiltonian matrix elements as integrals over antisymmetric many-electron basis functions required in standard molecular calculations (2,3). Construction and storage of the potentially very large Hamiltonian matrix that can arise in the spectral-product representation can be avoided by employing chemically relevant test functions and recursion methods in performing a unitary transformation to isolate its much smaller totally antisymmetric block. In this way, a physical Hamiltonian matrix is obtained from the non-interacting atomic energies, Heitler-London-like Coulomb and exchange terms, and contributions from spectral excitations which correspond to dispersion and polarization terms familiar from long-range pertubation theory (7).

Theoretical Formalism

The essential features of the formalism are described here for an aggregate of n hydrogen atoms, with more general results reported elsewhere (14). The orthonormal spectral-product basis in this case is the outer product row vector $\Phi(1, 2, \ldots n) = \left\{ \Phi^{(1)}(1) \otimes \Phi^{(2)}(2) \otimes \cdots \Phi^{(n)}(n) \right\}$ of n-electron product functions, each of which consists of products of n functions, one each taken from the indicated one-electron spin-orbital row vectors $\Phi^{(1)}(1), \Phi^{(2)}(2), \ldots \Phi^{(n)}(n)$. Although the n-electron functions so de-

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fined are not individually antisymmetric, the spectral-product basis is nevertheless complete for representations of antisymmetric states (7,8), and contains the totally antisymmetric representation once and only once (14).

The many-electron (Coulombic) Hamiltonian operator in the spectral-product basis is

$$\mathbf{H}(\boldsymbol{R}) = \sum_{\alpha=1}^{n} \left\{ \mathbf{H}^{(\alpha)} + \sum_{\beta=1}^{n} (\beta > \alpha) \, \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \right\}, \tag{1}$$

where

$$\mathbf{H}^{(\alpha)} = \mathbf{I}^{(1)} \otimes \mathbf{I}^{(2)} \otimes \cdots \mathbf{E}^{(\alpha)} \otimes \cdots \mathbf{I}^{(n)} \tag{2}$$

and

$$\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{I}^{(1)} \otimes \mathbf{I}^{(2)} \otimes \cdots \mathbf{v}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \otimes \cdots \mathbf{I}^{(n)} \tag{3}$$

are the indicated outer matrix products. Here, $\boldsymbol{R}$ specifies the entire aggregate atomic configuration, $\boldsymbol{R}_{\alpha\beta}$ is an atomic separation vector, and $\mathbf{I}^{(\alpha)}$ is the unit matrix and $\mathbf{E}^{(\alpha)}$ the diagonal matrix of energies for the atom α. As has been noted previously (14), the Hamiltonian matrix of Eq. (1) is rigorously additive in the pairwise interaction-energy matrices $\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ of Eq. (3). In the latter equation

$$\mathbf{v}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})^{\dagger} \cdot \mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta}), \tag{4}$$

where $\mathbf{D}^{(\alpha,\beta)}(\hat{\boldsymbol{R}}_{\alpha\beta})$ is comprised of products of rotation matrices (15,16) at the sites α and β, $\hat{\boldsymbol{R}}_{\alpha\beta}$ is the angular orientation of atom β relative to the site α, $R_{\alpha\beta}$ is the corresponding scalar separation, and $\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta})$ is a reduced interaction-energy matrix for the interacting pair oriented along a standard z coordinate axis. The latter matrix is given by the expression

$$\mathbf{v}^{(\alpha,\beta)}(R_{\alpha\beta}) = \frac{1}{2\pi^2} \int_{\mathbf{k}} d\mathbf{k} \, e^{ik_z R_{\alpha\beta}} \left\{ \alpha(\mathbf{k}) \otimes \beta(\mathbf{k})^{\dagger} \right\}, \tag{5}$$

with

$$\alpha(\mathbf{k}) = (e/k) \int_{\boldsymbol{r}_{\alpha}} d\boldsymbol{r}_{\alpha} \, \gamma^{(\alpha)}(\boldsymbol{r}_{\alpha}) \{1 - e^{i\mathbf{k}\cdot\boldsymbol{r}_{\alpha}}\}, \tag{6}$$

where

$$\gamma^{(\alpha)}(\boldsymbol{r}_{\alpha}) = \langle \Phi^{(\alpha)}(\mathbf{1}) | \delta^{(\alpha)}(\mathbf{1} - \boldsymbol{r}_{\alpha}) | \Phi^{(\alpha)}(\mathbf{1}) \rangle. \tag{7}$$

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Equations (5) to (7), which follow from a Fourier representation of the Coulombic interactions in the Hamiltonian operator (14), indicate that the atomic transition density matrices (17) of Eq. (7) provide the computational invariants required for construction of both the (Coulombic) response matrices of Eq. (6) and the reduced pair-interaction matrices of Eq. (5). Use of the familiar Rayleigh plane-wave expansion and of standard expressions for the resulting angular integrations (15) reduces evaluation of Eq. (5) to a single quadrature over the scalar k, whereas the integrals of Eqs. (6) and (7) can generally be evaluated in closed forms when Gaussian basis orbitals are employed.

Antisymmetric Subspace

Although the eigenfunctions obtained from the Hamiltonian $\mathbf{H}(R)$ of Eq. (1) span all irreducible representations of the symmetric group S_n, they do not necessarily transform irreducibly under the symmetry group defined by the complete set of commuting observables, and they are highly degenerate (14). To demonstrate formally that the totally antisymmetric or physical block of $\mathbf{H}(R)$ can be isolated and solutions obtained in symmetry-adapted form, the unitary transformation

$$\mathbf{U_S}(R)^\dagger \cdot \mathbf{H}(R) \cdot \mathbf{U_S}(R) \rightarrow \begin{pmatrix} \mathbf{H}_S^{(p)}(R) & \mathbf{0} \\ \mathbf{0} & \mathbf{H}_S^{(r)}(R) \end{pmatrix} \tag{8}$$

is employed. Here, the transformation $\mathbf{U_S}(R)$ is obtained from the diagonalization

$$\mathbf{U_S}(R)^\dagger \cdot \mathbf{S}(R) \cdot \mathbf{U_S}(R) \rightarrow n! \begin{pmatrix} \mathbf{I}^{(p)} & \mathbf{0} \\ \mathbf{0} & \mathbf{0}^{(r)} \end{pmatrix}, \tag{9}$$

where

$$\mathbf{S}(R) = (n!)^{1/2} \langle \Phi(1, 2, \ldots, n) | \hat{P}_A | \Phi(1, 2, \ldots, n) \rangle \tag{10}$$

is the matrix representative of the antisymmetrizer $\hat{P}_A$ (5), $n!$ is the redundancy of the spectral-product basis when antisymmetrized, (p) and (r) refer, respectively, to physical and remainder subspaces of $\Phi(1, 2, \ldots n)$, $\mathbf{I}^{(p)}$ and $\mathbf{0}^{(r)}$ are the unit and null matrices in the indicated subspaces, and the right-hand sides of Eqs. (8) and (9) are reached in the closure limit. In this limit, the eigenvalues and functions obtained from $\mathbf{H}_S^{(p)}(R)$ converge to values obtained in the prior antisymmetrized basis $\hat{P}_A \Phi(1, 2, \ldots n)$ when its $(n! - 1)$ redundant components are are removed $(7,14)$.

Although Eqs. (8) to (10) provide formal expressions to isolate the physical eigenstates from the unphysical states in which they can be embedded, and to correspondingly demonstrate equivalence with results obtained from prior antisymmetry (*14*), an efficient recursive scheme using appropriately chosen antisymmetrized starting functions is sufficient to construct $\mathbf{H}_S^{(p)}(R)$. Specifically, a transformation of the Hamiltonian matrix equivalent to that of Eq. (8) is obtained from the recurrence equations (*18*)

$$\beta_j(R)\, \mathbf{v}_{j+1}(R) = (\mathbf{H}^{(+)}(R) - \alpha_j(R)\, \mathbf{I}) \cdot \mathbf{v}_j(R) - \beta_{j-1}(R)\, \mathbf{v}_{j-1}(R), \quad (11)$$

where the column vectors $\mathbf{v}_j(R)$ for $j = 1, 2, \ldots p$ define a set of p orthonormal Krylov-Lanczos functions in the spectral-product basis, the recurrence coefficients $\alpha_j(R)$ and $\beta_j(R)$ give the diagonal and off-diagonal terms, respectively, of a p-dimensional tri-diagonal matrix which is unitarily equivalent to the Hamiltonian matrix $\mathbf{H}_S^{(p)}(R)$ of Eq. (8), and $\mathbf{H}^{(+)}(R)$ is the spectral-product Hamiltonian matrix supplemented with an additional row and column. The latter is constructed with an asymptotically ($R \to \infty$) correct antisymmetrized-product test function which insures that the totally antisymmetric subspace of the spectral-product representation is isolated in the Krylov-Lanczos basis, that the correct number of multiplet states and their exchange splittings are included in the atomic separation limit, and that an appropriate starting vector is provided for the recurrence of Eq. (11) (*14*). This iterative approach requires only sequential calculations of individual rows of the potentially very large Hamiltonian matrix in the spectral-product basis, avoiding construction and tabulation of the entire matrix at one time. Moreover, the resulting unitary transformation provides a much lower-dimension physically significant Hamiltonian matrix from the zeroth-order non-interacting atomic energies, first-order Coulomb and exchange terms, and higher-order contributions which correspond to dispersion and polarization terms familiar from long-range pertubation theory (*7,14*).

Computational Applications

Calculations of the lowest-lying attractive and repulsive states of the two-electron pair bond (H_2) illustrate the attributes of the formalism and the convergence achieved. In this case ($n_{total} = 2$), the spin functions factor out, there are no unphysical irreducible representations to contend with, and the development deals only with spatial functions which are symmetric (singlet) or antisymmetric (triplet) under electron transposition (*6*). The spectral-product representation spans these spatially symmetric and antisymmetric representations of the group S_2 once and only once, whereas the

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symmetric or antisymmetric forms of the basis are 2-fold redundant in the limit of closure. The absence of unphysical irreducible representations in this special case allows construction of solutions by direct diagonalization of the Hamiltonian matrix of Eq. (1) for comparisons with results obtained from the unitary-transformation [Eqs. (8) to (10)] and recursion [Eq. (11)] methods described above.

The spectral-product basis in this case corresponds formally to all products of discrete and continuum hydrogenic orbitals for the two atoms. To avoid dealing explicitly with continuum hydrogenic states, denumerable representational basis sets are employed in the calculations in the usual way (2). Even-tempered Gaussian functions $(s, p, d, f, \ldots)$ having exponents chosen to represent the lowest-lying atomic hydrogen orbitals accurately, and to span the corresponding Rydberg states and low-lying continua in the form of spectral packets (18), are employed in evaluating the matrix elements required in forming the spectral-product Hamiltonian matrix and the other integrals needed to implement the development.

Table I. Spectral Energies for Atomic Hydrogen.[a]

s-basis[b]	p-basis[b]	d-basis[b]	f-basis[b]
−0.499991	−0.124998	−0.055256	−0.026707
−0.124994	−0.053439	−0.011199	0.028807
−0.048465	0.025060	0.108901	0.187597
0.088668	0.274825	0.450236	0.617389
0.563368	0.986192	1.361055	1.748440
1.951139	2.880038	3.708833	4.791877
5.660465	7.854649	9.719458	
15.152536	21.314359	25.786063	
38.982050			
98.333482			
249.224098			
657.488778			

[a] Orbital energies (a.u.) obtained from diagonalization of the atomic hydrogen Hamiltonian employing the indicated basis sets.
[b] Basis sets employed are the most diffuse $(12s8p8d6f)$ hydrogenic orbitals constructed from 12 regularized even-tempered primitive Gaussian orbitals of each angular momentum symmetry (19), supplemented with two additional diffuse functions having exponents of 0.02786 and 0.01156.

In Table I are shown the spectra of atomic energies obtained for s, p, d and f orbitals constructed in even-tempered Gaussian basis sets (19), with orbital

exponents chosen so the discrete and lower continuum states are spanned by the numbers of orbitals shown for each angular momentum value. Although no systematic studies of orbital selection are reported here, it should be noted that considerable experience has been gained in this connection through previous studies of the discrete and continuum states of atoms and polyatomic molecules (18). The spectra of Table I are judged to be suitable for describing the charge distortions accompanying chemical bond formation in H_2 in the interval $R \approx 1$ to 5 a_0, to correctly describe wavefunction antisymmetry in this interval in the absence of explicit electron exchange terms, and to otherwise approximate spectral closure in this interval. Consequently, the atomic basis sets so devised are seen to be significantly larger than those commonly employed in molecular electronic structure calulations (2). This use of larger atomic basis sets in the spectral theory is ameliorated by the need to perform the electronic integral calculations of Eq. (7) once and only once, and by the associated avoidance of repeated evaluations of molecular integrals over antisymmetric basis states required in conventional developments.

In Figure 1 are shown as an example selected eigenvalues s_i of the metric matrix $S(R)$ of Eq. (10) for H_2, evaluated employing the $[sp]$ basis sets indicated in Table I. Only the fifty largest ($s_i \approx 2$) and the fifty smallest ($s_i \approx 0$) eigenvalues are shown as functions of the interatomic separation. The eigenstates of $S(R)$ corresponding to eigenvalues $s_i \approx 2$ refer to approximately antisymmetric states in the spectral-product basis, whereas those correponding to $s_i \approx 0$ refer to approximately symmetric states. On the other hand, states constructed in the prior antisymmetrized basis corresponding to the $s_i \approx 2$ values refer to linearly independent spatially antisymmetric states, while those corresponding to $s_i \approx 0$ values refer to linearly dependent combinations of the prior antisymmetrized basis. When the two-electron symmetric projector is employed in place of the antisymmetrizer, results identical to the foregoing are obtained, but with the states previously corresponding to $s_i \approx 2$ and $s_i \approx 0$ interchanging their identities.

A significant number of the eigenvalues of $S(R)$ depicted in Figure 1 evidently maintain their extreme values ($s_i \approx 0$ or 2) over the chemical interaction region ($R \approx 1$ to 5 a_0), whereas only a very few of these survive into the van der Waals region ($R \approx 5$ to 10 a_0). These behaviors are entirely in accord with the spatial characteristics of the spectral states corresponding to the eigenvalues of Table I employed in constructing $S(R)$, which have relatively small amplitudes at distances ≈ 5 to 10 a_0 from the atomic origins. Accordingly, the basis of Table I can be expected to give converged results in the chemical interaction region, and particularly at the equilibrium interatomic separation ($R = 1.40$ a_0), whereas alternative basis sets
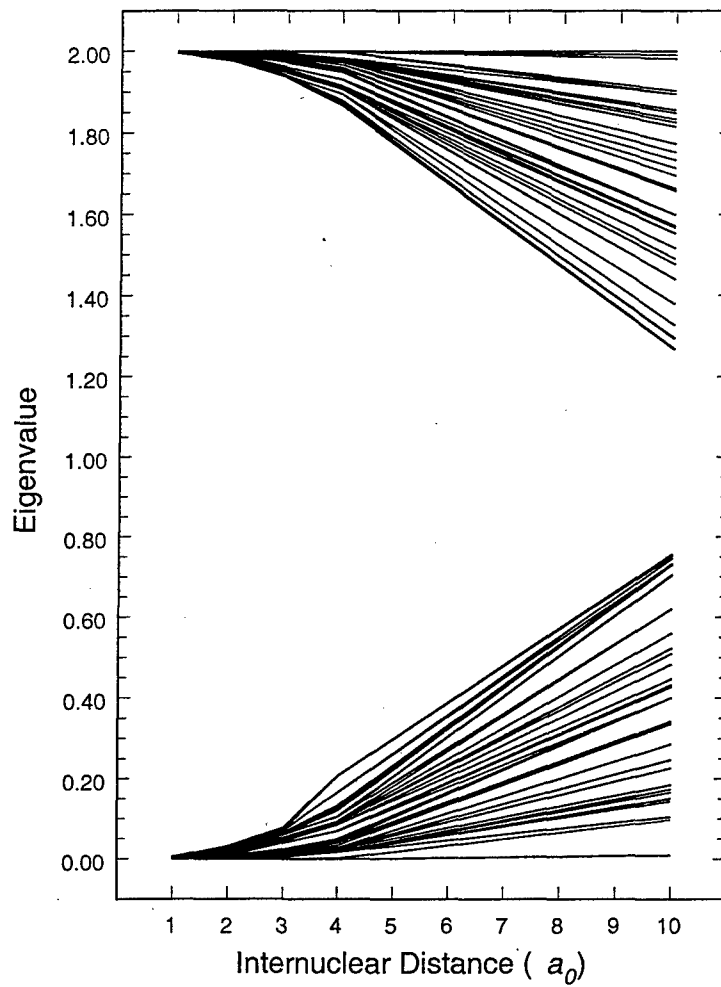
Figure 1–Eigenvalues s_i of the metric matrix of Eq. (10) for H_2, constructed in the $[sp]$ basis set of Table I as functions of interatomic separation $R(a_0)$. Values $s_i \approx 2$ refer to approximately antisymmetric eigenfunctions of electron coordinates constructed in the spectral-product basis, whereas values $s_i \approx 0$ refer to approximately symmetric functions of electron coordinates, as is discussed more fully in the text.

will likely be required to achieve closure at larger interatomic separations. These can be devised employing more diffuse Gaussian basis sets following previously described selection criteria (18).

Table II. Electron Pair-Bond Calculations.[a]

Basis[b]	Energy(a.u.)[c]	Binding(eV)[c]	$\langle \hat{P}_{12} \rangle$[c]	$(|\Phi^{(HL)}|^2)$[c]
		$^1\Sigma_g^+$ state		
[s]	−1.0096	+0.2618	+0.5255	+0.8052
[sp]	−1.0691	+1.8809	+0.8409	+0.9469
[spd]	−1.1140	+3.1027	+0.9525	+0.9872
[spdf]	−1.1384	+3.7667	+0.9847	+0.9967
Exact (20)	−1.1745	+4.7478	+1.0000	+1.0000
		$^3\Sigma_u^+$ state		
[s]	−0.5586	−12.0109	−0.6226	+0.2950
[sp]	−0.6641	−9.1400	−0.6905	+0.8078
[spd]	−0.7249	−7.4856	−0.9317	+0.9538
[spdf]	−0.7524	−6.7372	−0.9801	+0.9870
Exact (20)	−0.7842	−5.8737	−1.0000	+1.0000

[a] Values at $R = 1.40$ a_0 obtained from diagonalization of the Hamiltonian matrix of Eqs. (1) to (3) for H_2, or, equivalently, from the unitary transformation of Eqs. (8) to (10) in the text.
[b] Denotes the portion of the $(12s8p8d6f)$ basis set indicated in Table I employed in the calculation.
[c] Total and binding energies as indicated; $\langle \hat{P}_{12} \rangle$ refers to the expectation value of the electron transposition operator $\hat{P}_{12}$; $|\Phi^{(HL)}|^2$ is the norm of the Heitler-London function as represented in the spectral-product basis.

The spectra of Table I are employed in calculations of energies and expectation values for the lowest-lying $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states in H_2 at the equilbrium interatomic separation following the development of Eqs. (1) to (10). The total energies, binding energies, and expectation values of the electron transposition operator $\hat{P}_{12}$ for both states, shown in Table II, evidently converge monotonically to known values with increase in basis-set angular momentum. Similarly, the norms of the familiar singlet and triplet Heitler-London functions (4) represented in the spectral-product basis, also shown

in Table II, give additional indication of the closure achieved for exchange terms in this case. As indicated above, the values shown in Table II can be obtained directly from diagonalization of the spectral-product Hamiltonian of Eq. (1) or from the unitary transformation of Eqs. (8) to (10), with identical values resulting from the two procedures in the limit of closure. It is found in the smaller basis sets ([s], [sp]) indicated in Table I, however, that a relatively large block of the transformed Hamiltonian matrix of Eq. (8) is required in order to reproduce accurately the results obtained from the complete spectral-product Hamiltonian matrix. That is, the totally symmetric subspace in these cases is not completely isolated into a physical block $\mathbf{H}_S^{(p)}(\mathbf{R})$ in Eq. (8) which is necessarily small relative to the original spectral-product Hamiltonian matrix of Eq. (1). These observations serve to emphasize that the development of Eqs. (8) to (10) provides a formal proof of the convergence of the spectral method in the closure limit, rather than an optimal computational implementation of the approach.

The rate of convergence of the results of Table II with increasing angular momentum in the atomic basis is related to the nature of the charge distortions in H_2 consequent of bond and antibond formation at the equilibrium interatomic separation. In Figure 2 is shown the one-electron charge distribution in the plane of the two nuclei for the $^1\Sigma_g^+$ ground state obtained as indicated in the figure, with the undisturbed atomic charges of the two atoms in their $1s$ states subtracted out. Evidently, there is a distinct line of electronic charge connecting the two nuclei in this density difference map which provides sufficient attraction to form the bond in this case, in accordance with the predictions of the Hellmann-Feynman theorem. This additional "exchange charge," in an integrated amount equal to ≈ 0.25 electrons gathered from the outer-lying regions and concentrated between the two nuclei, is represented in the spectral-product basis by single-center overlap factors in the charge-density expression

$$\rho(\mathbf{r}) = \sum_{i,i'} \Gamma_{ii'} \phi_i^{(\alpha)}(\mathbf{r}) \phi_{i'}^{(\alpha)}(\mathbf{r})^* + \sum_{j,j'} \Gamma_{jj'} \phi_j^{(\beta)}(\mathbf{r}) \phi_{j'}^{(\beta)}(\mathbf{r})^*, \qquad (12)$$

where $\Gamma_{ii'}$ and $\Gamma_{jj'}$ form the one-electron density matrix in the orbital-product basis, with two-center differential overlap factors absent consequent of the orthonormality of the spectral-product fucntions. The exchange charge confined between the two atoms depicted in Figure 2 evidently requires the higher angular momentum functions of Table I for an accurate description of this accumulation upon bond formation, and also for corresponding convergence in the total energy and exchange factors of Table II.

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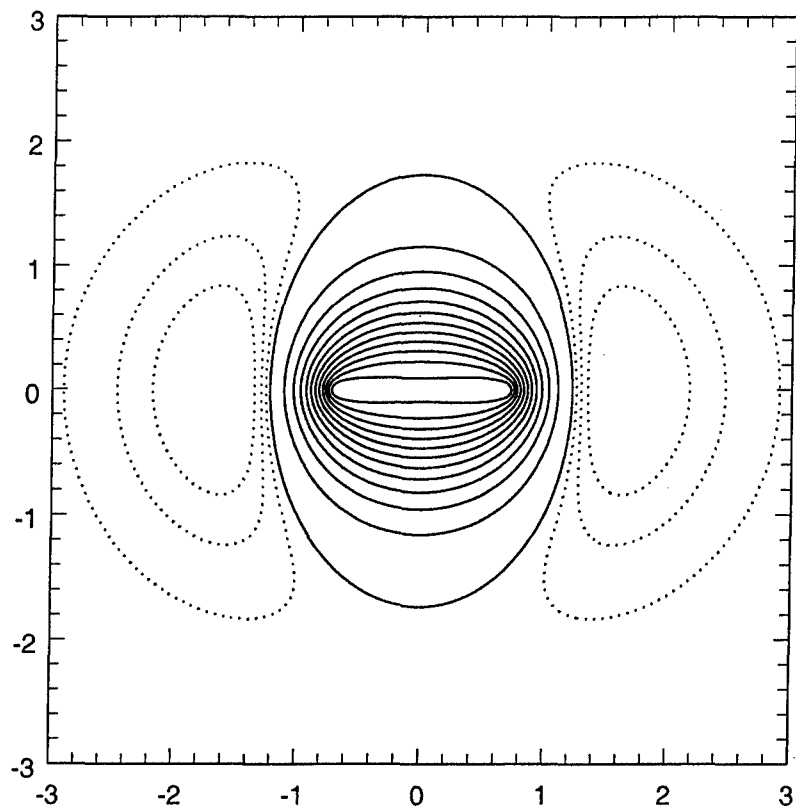
Figure 2–Charge-density difference map for H_2 in the plane of the two nuclei, depicting the accumulation of charge between the two atoms upon bond formation in the ground $^1\Sigma_g^+$ state. The quantity plotted is the total one-electron molecular change density obtained from a configuration-interaction calculation using the $[sp]$ basis of Table I, minus the charge density corresponding to the two unperturbed H atoms in their $1s$ ground states. The H_2 bond length is fixed at 1.40 a_0. The outermost solid contour represents a zero charge-density difference; successive solid contours are at charge-density difference intervals of 0.02 $a.u.$, with the innermost solid contour representing a charge-density difference of 0.1 $a.u.$; the outermost dashed contour corresponds to -0.003 $a.u.$ and the innermost dashed contour to -0.006 $a.u.$; a total of $\approx$ 0.25 additional electrons are accumulated in the bond.

The recursive projection procedure described above provides an alternative and potentially more efficient method for obtaining eigenstates than does the development of Eqs. (8) to (10). In the two-electron case, this procedure serves to separate the symmetric and antisymmetric subspaces spanned in the absence of unphysical representations, and can accelerate the convergence relative to that of Table II through incorporation of explicitly symmetric or antisymmetric test functions. In Figure 3 are shown $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potential energy curves in H_2 obtained from the recursive development and the basis states of Table I employing Heitler-London test functions in each case. These functions serve as appropriate chemical reference states at all interatomic separations, and also provide the starting functions required to generate recursively the correct permutation symmetries in the spectral-product subspaces. Evidently, the spectral-theory potential curves of Figure 3 converge rapidly in the chemical region ($R \approx 1$ to 5 a_0) as larger angular momentum values are included in the basis, the $[sp]$ limit already providing $\approx 90\%$ of the chemical bonding energy at the equilibrium interatomic separation, and the $[spd]$ limit providing $\approx 96\%$ of this value. Finally, although the basis of Table I is insufficient to accurately determine the exchange energy splitting in the van der Waals region ($R \approx 5$ to 10 a_0), the average value of the singlet and triplet energies obtained in the basis in this region is found to give accurate results for the leading ($C_6, C_8, \ldots$) van der Waals coeffcients.

Concluding Remarks

A new method is reported for calculating the adiabatic electronic wave functions and energies of molecules and other chemical aggregates. The spectral-product basis, formally comprising all simple products of the physical eigenstates of the individual atoms in the aggregate, gives a Hamiltonian matrix that is rigorously additive in pairwise-atomic interaction-energy matrices, greatly simplifying its evaluation relative to conventional methods which employ antisymmetrized basis states (2,3). In this approach, atomic structure calculations of electronic transition density matrices employed in constructing the Hamiltonian matrix need be performed once and only once, avoiding the repeated evaluations of many-electron matrix elements over antisymmetric molecular basis functions required in conventional potential-energy surface determinations. Procedures for isolating the totally antisymmetric subspace of the spectral-product basis are described which avoid construction and storage of the entire Hamiltonian matrix at one time, and which also largely overcome the symmetric-group complications which have hindered previous developments employing the atomic spectral-product representation (7-13).

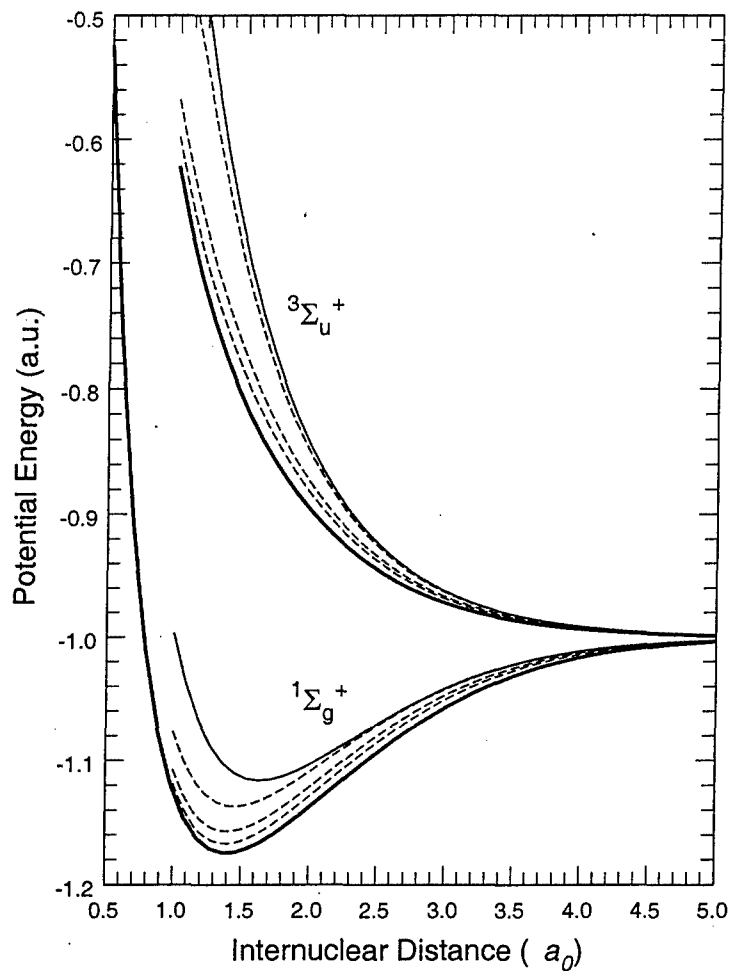Distribution A: Approved for public release; distribution unlimited.

Figure 3–Potential energy ($a.u.$) curves for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2 as functions of atomic separation $R(a_0)$. Light solid lines refer to Heitler-London values (4) and heavy solid lines to previously determined accurate values (20), whereas the dashed lines give the present results obtained from the recursion procedure indicated in the text employing the $[s]$, $[sp]$, and $[spd]$ basis states of Table I and Heitler-London test functions in each case.

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Applications of the formalism to the lowest-lying singlet and triplet states of H_2 illustrate the convergence achieved to results obtained from conventional methods, and demonstrate that prior basis-set antisymmetry is not necessarily required in *ab initio* molecular electronic structure calculations. The Hamiltonian matrix for any aggregate of interacting hydrogen atoms can be constructed from the calculated H_2 interaction-energy matrix employing the expressions of Eqs. (1) to (4) and explicit computational algorithims devised for their evaluation (*14*). Although applications to more complex many-electron atoms can encounter elaborate multiplet spectra, and possibly more significant charge distortions upon chemical bond formation, the algorithims for construction of the Hamiltonian matrix and isolation of its totally antisymmetric block described here for interacting hydrogen atoms are also applicable in such cases once the atomic matrices of Eqs. (5) to (7) have been evaluated.

The spectral theory offers an atomic-interaction-based strategy for constructing potential-energy surfaces which may provide a viable alternative to the largely unending series of molecular electronic structure calculations currently performed employing conventional methods. Additional studies are clearly required to develop the theory into a generally applicable computational approach to molecular structure determinations which can be employed to accurately predict the electronic energy changes and charge distortions consequent of chemical bonding in complex systems. Particularly required are methods for obtaining optimal representations of the atomic spectral eigenstates upon which the development is based, for the efficient assembly of individual elements of the Hamiltonian matrix in the spectral product basis, and for isolating its totaly antisymmetric subspace. These and related issues are presently under study, and progress in this program of research will be reported in due course elsewhere.

Acknowledgments

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