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P. W. Langhoff, J. D. Mills, J. A. Boatz, and G. G. Gallup

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14. ABSTRACT

In later papers,1,2 Per-Olov Löwdin addressed the issue of devising a satisfactory mathematical definition of molecular structure with characteristic clarity and insight, placing earlier related studies in the context of a common unifying perspective. He particularly noted the apparent impossibility of meaningful assignments of indistinguishable electrons to particular atomic nuclei in a molecular Hamiltonian, and the consequent absence of atoms, isomers, and spatial molecular symmetries on this basis.

In this contribution we address the assignments of electrons to atoms in molecules and provide a meaningful definition of chemical bonds between atoms from the perspective of representation theory. Use of an orthonormal (Eisenschitz-London) outer product of atomic spectral eigenstates as a representational basis in the absence of over-all aggregate electron antisymmetry allows meaningful assignments of electrons to particular atomic nuclei. Adiabatic (Born-Oppenheimer) molecular energies are obtained in this way in the form of a sum of physically significant atomic promotion energies and a pairwise-atomic sum of interaction energies, providing a quantum-mechanically-based quantitative definition of atoms and chemical bonds in molecules.

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Per-Olov Löwdin and the Coulomb Hamiltonian: Implications for Definition of Atoms and Bonds in Molecules

P.W. Langhoff,[1] J.D. Mills,[2] J.A. Boatz,[2] and G.G. Gallup[3]

[1] Department of Chemistry and Biochemistry, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0365

[2] Air Force Research Laboratory, 10 East Saturn Blvd., Edwards AFB, CA 93524

[3] Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588-0111

In later papers,[1,2] Per-Olov Löwdin addressed the issue of devising a satisfactory mathematical definition of molecular structure with characteristic clarity and insight, placing earlier related studies in the context of a common unifying perspective. He particularly noted the apparent impossibility of meaningful assignments of indistinguishable electrons to particular atomic nuclei in a molecular Hamiltonian, and the consequent absence of atoms, isomers, and spatial molecular symmetries on this basis. In this contribution we address the assignments of electrons to atoms in molecules and provide a meaningful definition of chemical bonds between atoms from the perspective of representation theory. Use of an orthonormal (Eisenschitz-London) outer product of atomic spectral eigenstates as a representational basis in the absence of over-all aggregate electron antisymmetry allows meaningful assignments of electrons to particular atomic nuclei. Adiabatic (Born-Oppenheimer) molecular energies are obtained in this way in the form of a sum of physically significant atomic promotion energies and a pairwise-atomic sum of interaction energies, providing a quantum-mechanically-based quantitative definition of atoms and chemical bonds in molecules.

I. INTRODUCTION

Although it is commonly agreed that "...all things are made of atoms...",[3] there appears to be no end of qualitative discusions of chemical bonds between atoms in a molecule,[4] or if such a notion even makes sense, or has a quantum-mechanical basis. Early opinions and attitudes concerning electron bonds between atoms range from "...more or less meaningless...",[5] and "...not a real thing...",[6] to "...the cornerstone of chemical thinking...".[7] By adopting a Hellmann-Feynman attitude, in which "...bond formation arises from attraction between positive nuclei and negative charge...",[8] bonds-between-atoms issues can be circumvented entirely. This attitude is in accord with modern quantum-chemical calulations, which largely employ atomic and/or molecular orbital representations, with calculated charge densities providing a basis for interpretive diagnostics.[7] In spite of this, a non-subjective definition of atoms and their bonds in molecules based on the quantum theory would seem to be a desirable objective.

When atoms form molecules or condensed matter atomic electrons "melt" into new quantum distributions which can retain to a greater or lesser degree the electronic charteristics of the combining species. Large electronegativity differences can lead to large charge tranfers, depleting electronic charge at one site and enhancing it at another, distoring therebye the inner atomic shells, which may nevertheless retain a certain pristine atomic character. It appears that electron indistinguishability and the required Pauli antisymmetry, more than any other single issue,[1,2] has frustrated attempts to define atoms and their bonds in molecules.[7,9,10] Here we report a quantum-theory-based definition of atoms and their bonds in molecules which takes these issues into account.

II. FORMAL THEORETICAL DEVELOPMENT

A. Atomic Spectral-Product Representation[11,12]

$$\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) \equiv \Big\{\boldsymbol{\Phi}^{(1)}(\mathbf{1}:\boldsymbol{R}_1)\otimes\boldsymbol{\Phi}^{(2)}(\mathbf{2}:\boldsymbol{R}_2)\otimes\cdots\boldsymbol{\Phi}^{(\mathrm{N})}(\boldsymbol{n}:\boldsymbol{R}_{\mathrm{N}})\Big\}_{\mathbf{o}}$$

where the row vectors $\boldsymbol{\Phi}^{(\alpha)}(\boldsymbol{i}:\boldsymbol{R}_\alpha)$ contain all the electronic states of the atom α located at position $\boldsymbol{R}_\alpha$, with all the electrons on this atom designated by the coordinate symbol $\boldsymbol{i}$. The subscript on the outer-product representation refers to the choice of an odometer ordering of the sequence of the N-atom states obtained from the indicated outer or tensor product of atomic states.

The S-P basis is complete in the limit of closure for descriptions of totally antisymmetric solutions of the Schrödinger equation in the absence of inter-atomic antisymmetry,[12] but also spans other irreducible representations of the symmetric group $S_{\mathrm{n_t}}$.[13–15]

B. Partitioning the Hamiltonian Operator

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

$$\hat{\mathrm{H}}^{(\alpha)}(\boldsymbol{i}) = \sum_{\mathrm{i}}^{\mathrm{n}_\alpha}\Big\{-\frac{\hbar^2}{2\mathrm{m}}\nabla_{\mathrm{i}}^2 - \frac{\mathrm{Z}_\alpha\mathrm{e}^2}{\mathrm{r}_{\mathrm{i}\alpha}} + \sum_{\mathrm{i'}=\mathrm{i}+1}^{\mathrm{n}_\alpha}\frac{\mathrm{e}^2}{\mathrm{r}_{\mathrm{ii'}}}\Big\}$$

$$\hat{\mathrm{V}}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta}) = \frac{\mathrm{Z}_\alpha\mathrm{Z}_\beta\mathrm{e}^2}{\mathrm{R}_{\alpha\beta}} - \sum_{\mathrm{i}}^{\mathrm{n}_\alpha}\frac{\mathrm{Z}_\beta\mathrm{e}^2}{\mathrm{r}_{\mathrm{i}\beta}} - \sum_{\mathrm{j}}^{\mathrm{n}_\beta}\frac{\mathrm{Z}_\alpha\mathrm{e}^2}{\mathrm{r}_{\mathrm{j}\alpha}} + \sum_{\mathrm{i}}^{\mathrm{n}_\alpha}\sum_{\mathrm{j}}^{\mathrm{n}_\beta}\frac{\mathrm{e}^2}{\mathrm{r}_{\mathrm{ij}}}$$

where $\boldsymbol{R}_{\alpha\beta} \equiv \boldsymbol{R}_\beta - \boldsymbol{R}_\alpha$, and all electron coordinates $(\mathbf{1},\mathbf{2},\ldots\boldsymbol{n})$ are assigned in accordance with the S-P representation, providing meaningful definitions of the foregoing atomic $\hat{\mathrm{H}}^{(\alpha)}(\boldsymbol{i})$ and atomic-interaction $\hat{\mathrm{V}}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}:\boldsymbol{R}_{\alpha\beta})$ operators in this basis.

C. Hamiltonian Matrix

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

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

where the atomic energy matrix is

$$\mathbf{H}^{(\alpha)} = \left\{ \mathbf{I}^{(1)} \otimes \mathbf{I}^{(2)} \otimes \cdots \mathbf{E}^{(\alpha)} \otimes \cdots \mathbf{I}^{(\mathbf{N})} \right\}_{\mathbf{o}}$$
$$= \begin{pmatrix} \mathbf{E}^{(\alpha)} & \mathbf{0} & \cdot & \cdot & \mathbf{0} \\ \mathbf{0} & \mathbf{E}^{(\alpha)} & \cdot & \cdot & \mathbf{0} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \mathbf{0} & \mathbf{0} & \cdot & \cdot & \mathbf{E}^{(\alpha)} \end{pmatrix}_{o}$$

and the interaction-energy matrix is

$$\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \left\{ \mathbf{I}^{(1)} \otimes \mathbf{I}^{(2)} \otimes \cdots \mathbf{V}_{\mathbf{d}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \otimes \cdots \mathbf{I}^{(\mathbf{N})} \right\}_{\mathbf{o}}$$
$$= \begin{pmatrix} \mathbf{V}_{\mathbf{d}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) & \mathbf{0} & \cdot & \cdot & \mathbf{0} \\ \mathbf{0} & \mathbf{V}_{\mathbf{d}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) & \cdot & \cdot & \mathbf{0} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \mathbf{0} & \mathbf{0} & \cdot & \cdot & \mathbf{V}_{\mathbf{d}}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \end{pmatrix}_{\mathbf{o}}$$

where the smaller-dimension matrix

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

involves only atomic-pair product functions. Faithful matrix representatives of the corresponding operators of Section B are evidently obtained which are universal computational invariants in the spectral-product basis. Since "odometer" ordering of the S-P basis is adopted, a row and column re-ordering algorithm ("o") must generally be employed to bring the atomic and interaction-energy matrices into canonical forms prior to their summation.

D. Exact Energy Expression

$$\mathbf{E}(\boldsymbol{R}) = \mathbf{U_H}^{\dagger}(\boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U_H}(\boldsymbol{R})$$

$$= \sum_{\alpha=1}^{\mathbf{N}} \mathbf{E}^{(\alpha)}(\boldsymbol{R}) + \sum_{\alpha=1}^{\mathbf{N}-1} \sum_{\beta=\alpha+1}^{\mathbf{N}} \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R})$$

where

$$\mathbf{E}^{(\alpha)}(\boldsymbol{R}) \equiv \mathbf{U_H}^{\dagger}(\boldsymbol{R}) \cdot \mathbf{H}^{(\alpha)} \cdot \mathbf{U_H}(\boldsymbol{R})$$

$$\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}) \equiv \mathbf{U_H}^{\dagger}(\boldsymbol{R}) \cdot \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \cdot \mathbf{U_H}(\boldsymbol{R})$$

Diagonal terms of atomic promotion energies $\mathbf{E}^{(\alpha)}(\boldsymbol{R})$:

$$\{\mathbf{E}^{(\alpha)}(\boldsymbol{R})\}_{\mathbf{gg}} \equiv \sum_{\mathbf{k}=1}^{\mathbf{N_s}} \sum_{\mathbf{l}=1}^{\mathbf{N_s}} \{\mathbf{U_H}^{\dagger}(\boldsymbol{R})\}_{\mathbf{gk}} \{\mathbf{H}^{(\alpha)}\}_{\mathbf{kl}} \cdot \{\mathbf{U_H}(\boldsymbol{R})\}_{\mathbf{lg}}$$

$$= \sum_{\mathbf{k}=1}^{\mathbf{N_s}} \{\mathbf{H}^{(\alpha)}\}_{\mathbf{kk}} |\{\mathbf{U_H}(\boldsymbol{R})\}_{\mathbf{kg}}|^{\mathbf{2}}$$

Diagonal terms of interaction energies: $\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R})$:

$$\{\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R})\}_{\mathbf{gg}} \equiv \sum_{\mathbf{k}=1}^{\mathbf{N_s}} \sum_{\mathbf{l}=1}^{\mathbf{N_s}} \{\mathbf{U_H}^{\dagger}(\boldsymbol{R})\}_{\mathbf{gk}} \{\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{\mathbf{kl}} \cdot \{\mathbf{U_H}(\boldsymbol{R})\}_{\mathbf{lg}}$$

$$= \sum_{\mathbf{k}=1}^{\mathbf{N_s}} \{\mathbf{E}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})\}_{\mathbf{kk}} |\{\mathbf{U_H}^{(\alpha,\beta)}(\boldsymbol{R})\}_{\mathbf{kg}}|^{\mathbf{2}}$$

The total molecular electronic energy is seen to be a sum of atomic promotion energies for the constituent atoms and a sum of bond energies, each of which are computable weighted averages over atomic spectral energies or diatomic potential energy curves.

III. COMPUTATIONAL IMPLEMENTATION

A. The Spectrum of the S-P Hamiltonian Matrix

Computational implementations of the foregoing formal development must overcome the troublesome nature of the spectrum of the Hamiltonian matrix in the spectral-product representation.[12] Issues to be overcome in this connection include the presence of so-called non-Pauli or non-totally-antisymmetric solutions of the Schrödinger equation spanned by the S-P representation, the requirement of spectral closure to achieve precise antisymmetry in the Pauli or totally antisymmetric solutions, clarification of the apparent absence of so-called charge-transfer or ionic terms in S-P representations, which would seem to include only covalent-like structures, the apparent absence of energy-coupling between atomic-product states having different spin configurations, and other technical issues related to the largely unfamiliar nature of an atomic eigenstate-product representation.

B. Exact-Pair Development in Finite S-P Representations

The aforementioned technical difficulties have been largely overcome in a series of publications which describes these issues quantitatively, providing expressions identical in form to those given in the foregoing Section II in finite atomic S-P representations.[16−23] This implementation of the theory employs an aggregate Hamiltonian matrix identical in appearance to that of the foregoing Section II-C, wherein the pair-interaction terms are constructed in antisymmetric atomic-product pair states, whereas the exact energy expressions of Section II-D are entirely unchanged in appearance. Accordingly, the atomic promotion and bonding energies are calculated employing modifications of largely standard means with a code suite devised for this purpose.[23]

IV. ILLUSTRATIVE PEDOGOGICAL EXAMPLES

A. Charge Transfer in the S-P Representation

Figure 1 depicts potential energy curves for the LiH molecule, in which the presence of charge-transfer configurations ($H^- + Li^+$) are widely regarded as giving rise to the indicated avoided crossings in the $^1\Sigma^+$ states. The calculated results in Figure 1, however, do not include explicit charge-transfer configurations, but rather represent these terms with atomic Rydberg-state products, which combine to form the charge-transfer term and give rise to the molecular Rydberg curves also depicted.

B. Total Molecular Electronic Energy Calculations

Figure 2 depicts potential enegy curves for the H_3 molecule in symmetric collinear arrangement calcuated in a series of model atomic-product representations, in comparison with corresponding conventional valence-bond results constructed in the largest representation employed. Evidently, the S-P results converge smoothly but not montonically to the conventional valence-bond results as the size of the basis set is increased.

C. Atomic Promotion and Bond Energies

Table 1 and Figures 3 and 4 depict the atomic promotion and bond energies for the ground-state obtained from the (1s2s) S-P representation employed in the calculations of Figure 2. The promotion energies are seen to vary smoothly from their large-R limiting 1s values as 2s promotion comes into play at shorter R. The $V^{(ab)}(R)=V^{(bc)}(R)$ energies exhibit increasing bonding at shorter R, whereas the $V^{(ac)}(R)$ bonding energy exhibits very weak bond enhancement at $R \approx 3$ Bohr, presumably due to the presence of the 2s promotion depicted in the $E^{(c)}(R)$ variation.

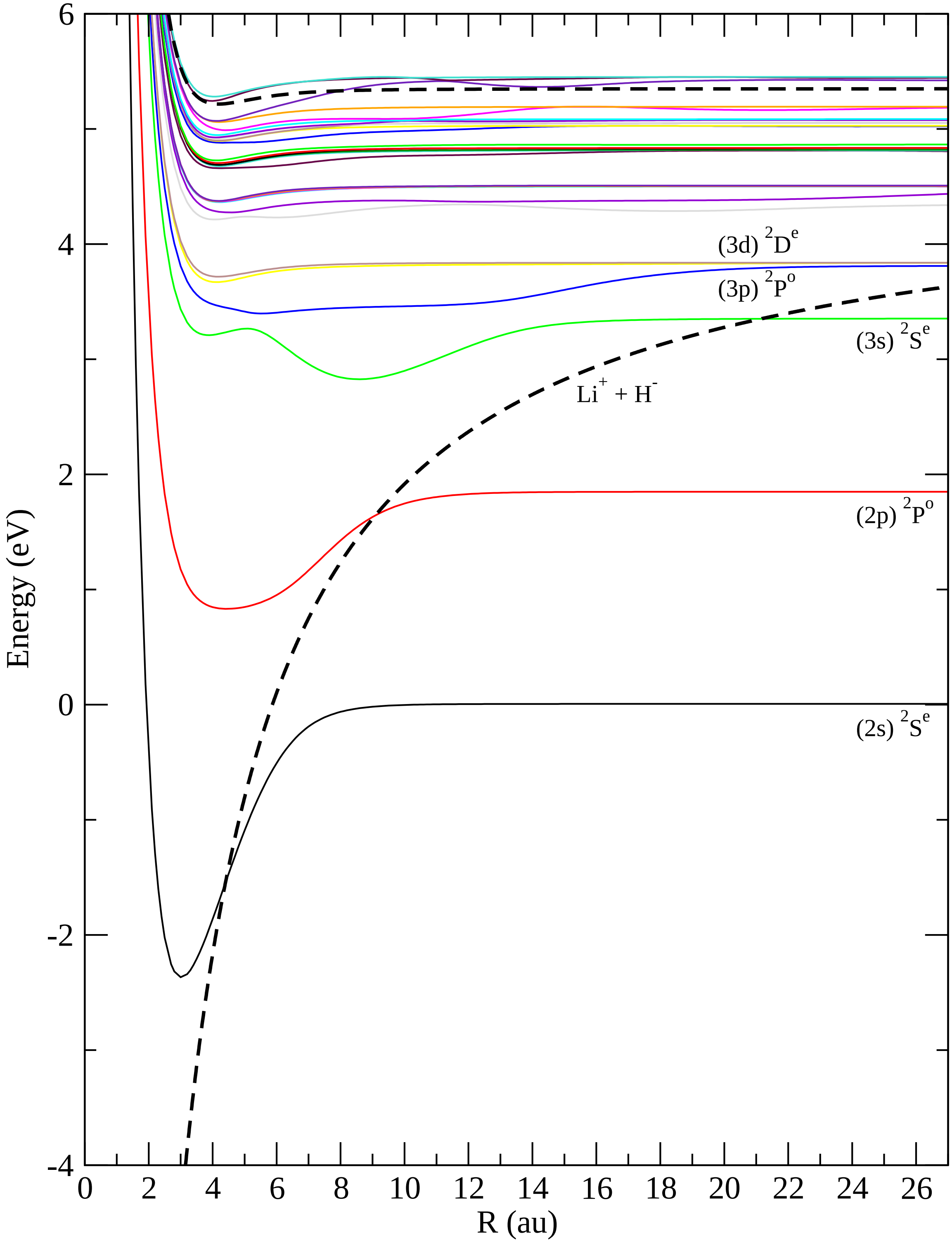

Figure 1: Potential energy curves for $^1\Sigma^+$ states in LiH calculated employing even-tempered Slater-orbital basis sets in the absence of explicit charge-transfer configurations.

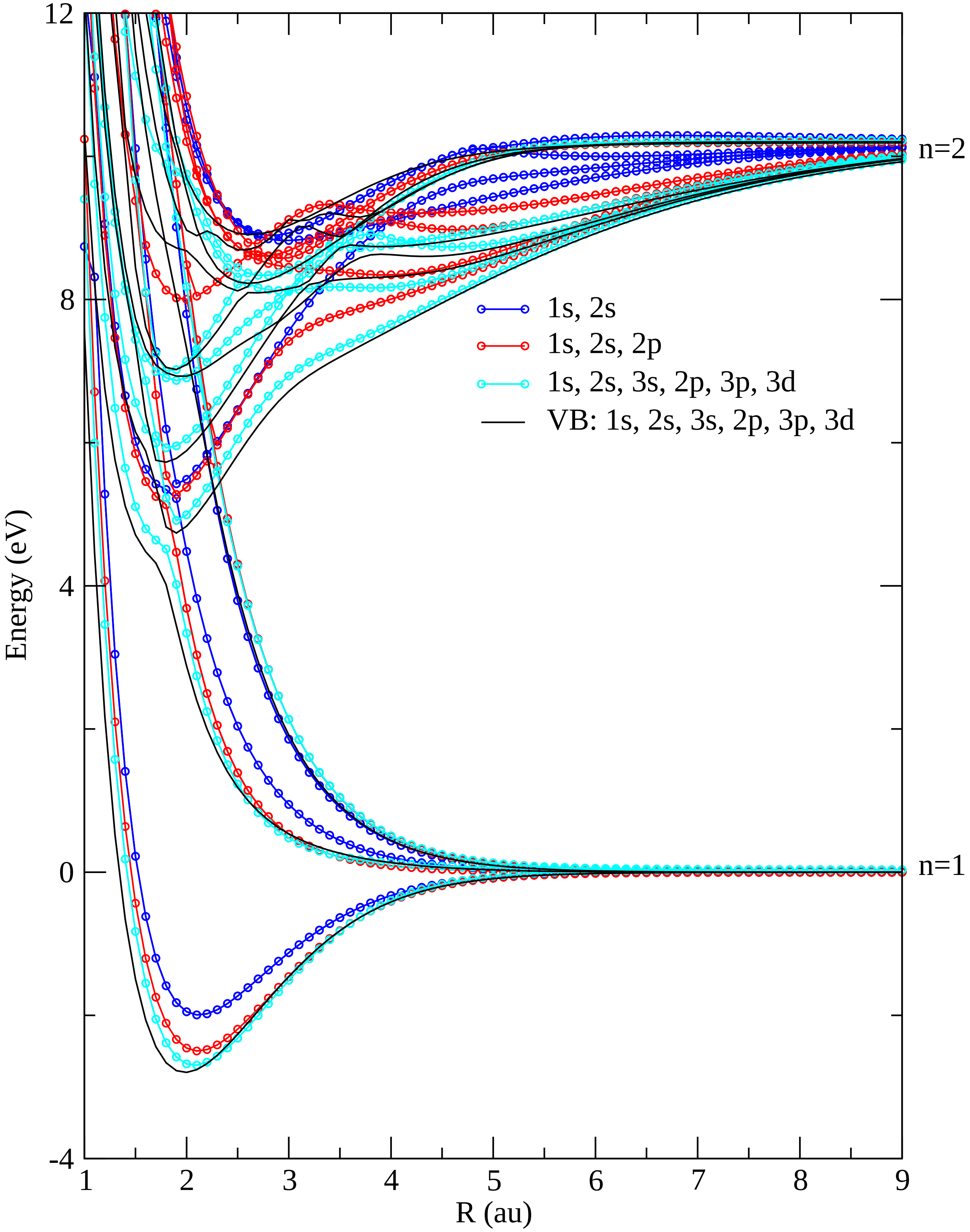

Figure 2: Convergence of exact-pair calculations of doublet and quartet potential energy curves in H_3 in symmetric collinear arrangement.

Table 1. Atomic Promotion and Pairwise Bond Energies[a,b]

R (Bohr) -	1.0	2.0	3.0	4.0	5.0	10.0
			Ground-State Doublet[c]			
$E^{(a)}(R)$ -	1.14	0.076	0.034	0.021	0.015	0.00
$E^{(b)}(R)$ -	0.46	0.020	0.134	0.091	0.046	0.00
$V^{(ab)}(R)$ -	3.52	-1.11	-0.750	-0.25	-0.09	0.00
$V^{(ac)}(R)$ -	2.91	0.19	-0.025	-0.01	0.00	0.00
$E_{total}(R)$ -	12.7	-1.86	-1.26	-0.38	-0.10	0.00

[a] Values obtained from the expressions of Section II-D of the text in the case of the (1s,2s) atomic-product representation employed in construction of the potential energy curves depicted in Figure 2. The atom labelled b is in center of the H_3 molecule.

[b] All energy values reported in units of electron volts (eV), setting the ground-state atomic orbital energy to zero ($E_{1s} = 0$). The promotion energy of the atom labelled c is $E^{(c)}(R) = E^{(a)}(R)$ and the bond energy $V^{(bc)}(R) = V^{(ab)}(R)$, where R refers to the scalar nearest atomic neighbor separation.

[c] The pair-interaction energy matrices of Section II-C are symmetrized in the coordinates of the nuclei a and c to the reflect the inversion symmetry of H_3 in symmetric collinear arrangements. The total Hamiltonian matrix is invariant to this procedure, allowing incorporation of molecular symmetry in the development quite generally. The three atomic promotion energies and three bond energies of the Table and Figures 3 and 4 correctly sum to the total potential energy curve of Figure 2.

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ATOMS AND THEIR INTERACTIONS IN MOLECULES

“...all things are made of atoms...” - R.P. Feynman

“...bonds are the cornerstone of chemical thinking...” - R. Bader

“...bonds are more or less meaningless...” - R.S. Mulliken

“...a chemical bond is not a real thing...” - C.A. Coulson

“...bonds are from attraction of nuclei & electrons...” - J.C. Slater

“...there is no meaningful assignment of electrons to particular nuclei in a molecule...” - P.-O. Löwdin

QM DEFINITION OF ATOMS AND BONDS IN MOLECULES

Assignments of electrons to nuclei - JCP 100, 1974 (1996)

Atomic Product Basis:

$$\boldsymbol{\Phi}(\boldsymbol{r}:\boldsymbol{R}) \equiv \left\{\boldsymbol{\Phi}^{(1)}(\boldsymbol{1}:\boldsymbol{R}_1) \otimes \boldsymbol{\Phi}^{(2)}(\boldsymbol{2}:\boldsymbol{R}_2) \otimes \cdots \boldsymbol{\Phi}^{(\mathrm{N})}(\boldsymbol{n}:\boldsymbol{R}_\mathrm{N})\right\}_{\mathbf{o}}$$

Hamiltonian Matrix:

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

Energy Expression: $\mathbf{E}(\boldsymbol{R}) = \mathbf{U_H}^{\dagger}(\boldsymbol{R}) \cdot \mathbf{H}(\boldsymbol{R}) \cdot \mathbf{U_H}(\boldsymbol{R})$

$$= \sum_{\alpha=1}^{\mathbf{N}} \mathbf{E}^{(\alpha)}(\boldsymbol{R}) + \sum_{\alpha=1}^{\mathbf{N}-1} \sum_{\beta=\alpha+1}^{\mathbf{N}} \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R})$$

Figure 2. Atomic Promotion Energies (eV)

Figure 3. Atomic-Pair Bond Energies (eV)

Atomic Promotion Energy - $\mathbf{E}^{(\mathbf{a})}(\boldsymbol{R}) = \mathbf{E}^{(\mathbf{c})}(\boldsymbol{R})$

Atomic Promotion Energy - $\mathbf{E}^{(\mathbf{b})}(\boldsymbol{R})$

$\mathbf{E}^{(\mathbf{a})}(\boldsymbol{R}) = \mathbf{E}^{(\mathbf{c})}(\boldsymbol{R})$

$\mathbf{E}^{(\mathbf{b})}(\boldsymbol{R})$

Atomic-Pair Bond Energy - $\mathbf{V}^{(\mathbf{ab})}(\boldsymbol{R}) = \mathbf{V}^{(\mathbf{bc})}(\boldsymbol{R})$

Atomic-Pair Bond Energy - $\mathbf{V}^{(\mathbf{ac})}(\boldsymbol{R})$

$\mathbf{V}^{(\mathbf{ab})}(\boldsymbol{R}) = \mathbf{V}^{(\mathbf{bc})}(\boldsymbol{R})$

$\mathbf{V}^{(\mathbf{ac})}(\boldsymbol{R})$

R(au)

R(au)

R(au)

R(au)