

## Modified Generalized Valence-Bond Method: A Simple Correction for the Electron Correlation Missing in Generalized Valence-Bond Wave Functions; Prediction of Double-Well States for Cr<sub>2</sub> and Mo<sub>2</sub>

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A new method for wave functions especially suited to studies of transition-metal systems is proposed and applied to H<sub>2</sub>, N<sub>2</sub>, Cr<sub>2</sub>, and Mo<sub>2</sub>, where it provides accurate bond energies and bond distances. The resulting potential curve for *ground state* Cr<sub>2</sub> has a double well, and experiments to detect this unusual feature are suggested. The Mo<sub>2</sub> studies lead to an assignment for the long-lived emitter observed in matrix studies (it is the  $\delta\delta^*{}^3\Sigma_u^+$  state).

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In the last decade, much progress has been made in learning how to obtain accurate bond energies with *ab initio* wave functions. Unfortunately, the requirements in both basis set and level of correlation (number of configurations) are quite severe, and simplifications to allow practical calculations can easily lead to large errors. Thus, for Cr<sub>2</sub>, it has been estimated<sup>1</sup> that 57 million configurations would be required just to obtain a bond energy of 0.6 eV (the experimental value<sup>2</sup> is  $2.0 \pm 0.3$  eV)! In this paper we examine the origin of this electron-correlation problem for bond energies and find that the dominant problem is the large error in describing *atomic* electron affinities. Armed with this insight, we develop a simple modification of the generalized valence-bond (GVB) method in which certain atomic Coulomb integrals are modified so as to provide the correct atomic electron affinities. With this modified GVB method (MGVB), we obtain not only accurate bond energies and bond distances but also accurate shapes for the potential curves.

First we consider what electron correlation effects are missing from *ab initio* GVB wave functions. At large distances a homonuclear covalent bond has the form

$$\Psi_{\text{cov}} = [\phi_l(1)\phi_r(2) + \phi_r(1)\phi_l(2)](\alpha\beta - \beta\alpha), \quad (1)$$

where  $\phi_l$  and  $\phi_r$  are singly occupied orbitals localized on the left and right centers, respectively. At small distances (when the  $\phi_l$  and  $\phi_r$  orbitals overlap) the GVB wave function<sup>3</sup> becomes

$$\Psi_{\text{GVB}} = (\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha), \quad (2)$$

where (if we ignore normalization)

$$\phi_a = \phi_l + \lambda\phi_r, \quad (3)$$

$$\phi_b = \phi_r + \lambda\phi_l$$

(and where  $\phi_l$  and  $\phi_r$  have changed somewhat from the atomic shape). Expanding (2) in terms of (3) leads to

$$\Psi_{\text{GVB}} = C_c\Psi_{\text{cov}} + C_i\Psi_{\text{ion}}, \quad (4)$$

where

$$\Psi_{\text{ion}} = [\phi_l(1)\phi_l(2) + \phi_r(1)\phi_r(2)](\alpha\beta - \beta\alpha). \quad (5)$$

Thus, intrinsic to the GVB description is the superposition of *ionic* terms containing *doubly occupied* atomic orbitals with the *covalent* terms involving *singly occupied* atomic orbitals. Because of the doubly occupied atomic orbitals, the ionic terms involve 1 to 3 eV more correlation error than the covalent terms, which leads to a bond that is too weak and too long. In order to establish the merit of this view concerning the dominant correlation error in the GVB wave function, we have developed a procedure for correcting the atomic correlation error in the ionic part of the GVB wave function and applied this modified GVB procedure to H<sub>2</sub>, N<sub>2</sub>, Cr<sub>2</sub>, and Mo<sub>2</sub>.

For H<sup>-</sup>, the optimum Hartree-Fock (HF) wave function<sup>4</sup> has an energy 1.39 eV higher than the exact wave function,<sup>5</sup> whereas the corresponding wave functions for H<sup>+</sup> and H are exact. Thus, by correcting the atomic self-Coulomb energy<sup>6</sup>

$$J_{ii}^M = J_{ii}^{AI} - 1.39, \quad (6)$$

we obtain the exact limits at infinity for both wave functions (1) and (5). (Here M denotes modified and AI *ab initio*.) For finite distances we use the correction (6) but evaluate all other atomic and molecular integrals exactly, leading to the potential curve in Fig. 1(a). From Table I we see that this simple correction to GVB leads to accurate results (bond-energy error of 0.08 eV<sup>10</sup>).

As a further test of MGVB, we carried out analogous calculations on N<sub>2</sub> (here the correlation corrections are based on a comparison between experimental<sup>5,11</sup> and calculated<sup>4</sup> energies for N<sup>+</sup>, N, and N<sup>-</sup>). (In this case, writing the GVB wave function in terms of natural orbitals leads to a total of fourteen spatial configurations.) The results in Fig. 1(b) and Table I indicate a similar high accuracy (bond-energy error of 0.1 eV)<sup>12</sup> for this very simple MGVB wave function (with *no* adjustable parameters).

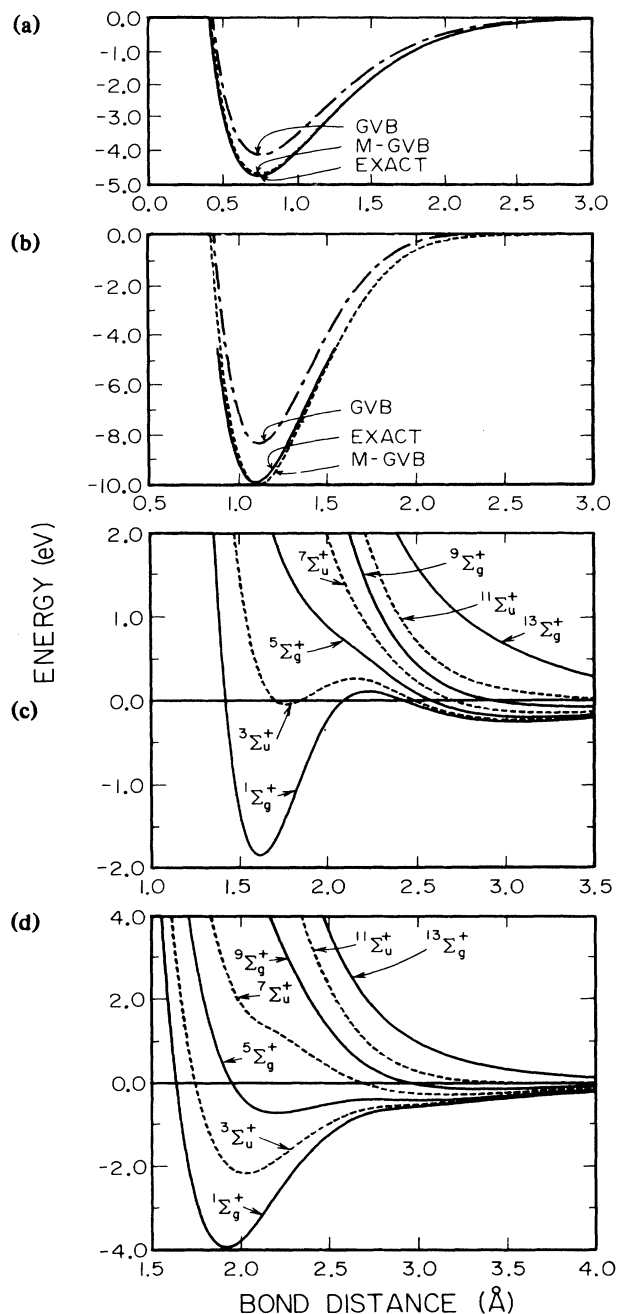


FIG. 1. Potential curves for (a)  $H_2$ , (b)  $N_2$ , (c)  $Cr_2$ , and (d)  $Mo_2$ . In (a) and (b), the results from MGVB are compared with *ab initio* GVB and with exact results (for  $N_2$  the experimental results are available only out to 1.56 Å). In (c) and (d), the MGVB results are shown for all spin states dissociating to the ground-state atoms.

Next we consider the implications for  $Cr_2$  and  $Mo_2$ , systems for which all six valence orbitals of each atom must be allowed to make bonds. Each bond consists of covalent and ionic pieces as in (4) so that the total

wave function contains the product of six covalent bonds, involving ground-state neutral configurations,

$$(s^1d^5)_l-(s^2d^5)_r, \quad (7)$$

plus terms for the ionic part of the *s-s* bond,

$$(s^0d^5)_l-(s^2d^5)_r, \quad (8)$$

and terms for the ionic part of the *d-d* bonds,

$$(s^1d^4)_l-(s^1d^6)_r. \quad (9)$$

This analysis suggests why  $Cr_2$  leads to such a severe problem for the *ab initio* wave functions. The correlation error in the HF description of a  $(4s)^2$  pair is about 1 eV, whereas the correlation error for a single  $(3d)^2$  pair is about 3 eV. The total error in the HF energy of configurations (8) and (9) relative to (7) at  $R = \infty$ ,

$$\begin{aligned} \delta E(s^0d^5) + \delta E(s^2d^5) - 2\delta E(s^1d^5) \\ = \delta(\text{I.P.})_s - \delta(\text{E.A.})_s, \end{aligned} \quad (10)$$

$$\begin{aligned} \delta E(s^1d^4) + \delta E(s^1d^6) - 2\delta E(s^1d^5) \\ = \delta(\text{I.P.})_d - \delta(\text{E.A.})_d, \end{aligned} \quad (11)$$

where  $(\text{E.A.})_s$  and  $(\text{I.P.})_s$  denote the *s*-electron affinity and ionization potential, respectively, can be corrected in the GVB wave function by modification of just the *s-s* and *d-d* one-center self-Coulomb terms ( $\delta J_{ss}^{Cr} = -0.67$  eV,  $\delta J_{ss}^{Mo} = -0.43$  eV,  $\delta J_{dd}^{Cr} = -2.55$  eV, and  $\delta J_{dd}^{Mo} = -1.59$  eV) and evaluation of all other integrals exactly.

The results for  $Cr_2$  and  $Mo_2$  are shown in Figs. 1(c) and 1(d) and in Table I, where we see that the MGVB wave function leads to good agreement with experiment. For larger bond distances ( $R > 3$  Å), the MGVB results are in excellent agreement with the previous *ab initio* calculations<sup>13</sup> (where the van der Waals configurations included all important electron-correlation effects for the *s-s* bonds that dominate in this region); however, for short distances (dominated by *d-d* bonding), the MGVB calculations account for an extra 2.5 eV of bonding in  $Mo_2$  and an extra 4.3 eV in  $Cr_2$ .

Particularly noteworthy for the MGVB potential-energy curves of  $Cr_2$  is the prediction of a double minimum. Just as explained earlier<sup>13</sup> for  $Mo_2$ , the long-bond form has a single  $4s-4s$  bond with the *d* shells coupled (antiferromagnetically) into a net singlet state, whereas the short-bond form has five covalent *d* bonds. Although the outer minimum is bound by only<sup>13</sup> 0.3 eV ( $R_e = 3.06$  Å), we find a 0.4-eV barrier to conversion to the short-bond form, and hence it should be possible to design experiments to detect the long-bond form of  $Cr_2$ . For example, photodecomposition of  $Cr_2$  isolated in an inert-gas matrix could lead to reassociation in which some molecules would remain in the long-bond state. Indeed, all states with spin  $S \geq 1$  have  $R_e > 3$  Å. Thus, experiments

TABLE I. Comparison of theoretical results (MGVB) with experiment.

	$R_e$ Bond distance ( $\text{\AA}$ )		$D_e$ Bond energy (eV)	
	MGVB	Expt.	MGVB	Expt.
H <sub>2</sub>	0.75	0.741 <sup>a</sup>	4.67	4.75 <sup>a</sup>
N <sub>2</sub>	1.12	1.098 <sup>a</sup>	10.00	9.91 <sup>a</sup>
Cr <sub>2</sub>	1.61	1.68 <sup>b</sup>	1.86	2.0 ± 0.3 <sup>b</sup>
Mo <sub>2</sub>	1.92	1.93 <sup>b</sup>	3.94	4.2 ± 0.2 <sup>b</sup>

<sup>a</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1979), Vol. 4.  $D_e = D_0 + \frac{1}{2}hc\omega_e$  was used to calculate  $D_e$ .

<sup>b</sup>References 2 and 7-9.

under high magnetic fields might aid sensitivity to detection of long-bond states.

For Mo<sub>2</sub> the ground state and lowest triplet have an inflection in the long-bond region but no second minimum, while the quintet state exhibits a double well. The states with  $S \geq 3$  prefer the long-bond form. In studies of the fluorescence from matrix-isolated Mo<sub>2</sub>, Pellin, Foosnaes, and Gruen<sup>14</sup> observed a very long-lived fluorescence ( $\tau = 2.1$  to 6.3 msec for two sites in Ar;  $\tau = 0.70$  to 1.44 msec for two sites in Kr) with a 0-0 transition at 1.68 to 1.71 eV (dependent upon site and matrix) resulting from excitation at 2.5 eV, and they were able to assign the final state for this transition as the ground state ( $X^1\Sigma_g^+$ ). In Fig. 1(d) we see that the only excited electronic state available for this transition is a  $^3\Sigma_u^+$  and that the energy of this state is at 1.77 eV, in excellent agreement with experiment. The fact that the emission rate is 3 times faster in Kr than in Ar is consistent with the expected enhanced spin-orbit coupling in  $^3\Sigma_u^+$  due to the Kr matrix. This triplet state has the character of a  $\delta\delta^*$  excited state and hence corresponds to the first experimental observation of a  $\delta\delta^*$  triplet state (long sought in various rare-earth-metal dimer complexes, e.g., Cl<sub>4</sub>RE = RECl<sub>4</sub><sup>2-</sup>).<sup>15</sup>

Recent calculations<sup>16</sup> using local spin-density (LSD) formalisms have given accurate results for  $R_e$  for both Cr<sub>2</sub> and Mo<sub>2</sub> (errors less than 0.1  $\text{\AA}$ ), somewhat less accuracy for bond energies (too strong by 0.5 to 1.0 eV), but no double well for Cr<sub>2</sub> (or Mo<sub>2</sub>). We believe that this lack of a double well arises from the necessity in LSD of using unrestricted Hartree-Fock-type wave functions in which incorrect spin contamination increases rapidly as a function of distance. This apparently is not a major problem at  $R_e$  (1.68  $\text{\AA}$ ) but for the long-bond form of Cr<sub>2</sub> (3.06  $\text{\AA}$ ) it could be quite serious. Indeed, Cr<sub>2</sub> would be an excellent test system for the further development of the LSD formalism since proper description of short-bond versus long-bond forms and correct description of the higher-spin

states (favoring long bond) would provide challenges that should dramatize any flaws in the methodology.

The MGVB method described here involves a simple correction of the one-center self-Coulomb integrals to match the experimental difference between electron affinity and ionization potential. This yields accurate potential curves for the various states dissociating to ground-state atoms. We are currently in the process of developing an analogous (but more complicated) approach where various one-center two-electron integrals are adjusted to fit the atomic excitation energies, ionization potentials, and electron affinities, and are used in molecular GVB calculations with all multicenter integrals calculated *ab initio*. This overall approach smacks of semiempiricism; however, we believe that it should be thought of in terms of modification of the valence Hamiltonian to account for high-level electron correlation effects as in the work of Takada and Freed.<sup>17</sup> This procedure in MGVB is also somewhat analogous to the procedure used in local density calculations where the results of the fully correlated electron gas are built into the Hamiltonian used for molecular calculations.

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<sup>2</sup>A. Kant and B. Strauss [*J. Chem. Phys.* **45**, 3161 (1966)] reported an experimental bond energy of  $1.6 \pm 0.3$  eV based on old assumptions of  $R_e$ ,  $\omega_e$ , and spin. With  $R_e = 1.68$   $\text{\AA}$ ,  $\omega_e = 470$   $\text{cm}^{-1}$ , and an electronic degeneracy of 1, the experimental bond energy becomes  $2.0 \pm 0.3$  eV.

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<sup>4</sup>The basis set used for H is a 6s1p primitive set of Gauss-

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<sup>5</sup>All electron affinities are from H. Hotop and W. C. Lineberger [*J. Phys. Chem. Ref. Data* **4**, 539 (1975)]. Recent work by C. S. Feigerle, R. R. Corderman, S. V. Bobashev, and W. C. Lineberger [*J. Chem. Phys.* **74**, 1580 (1981)] has led to  $s$ -electron affinities of 0.667 and 0.747 eV for Cr and Mo, respectively, and these values are used for discussions in the text. Since the experimental  $d$ -electron affinity is not known for Cr and Mo, we assume that the HF errors for  $E(s^1d^6) - E(s^1d^5)$  and for  $E(s^0d^6) - E(s^0d^5)$  are equal.

<sup>6</sup>In making this correction, we do the equivalent of the following: (1) symmetrically orthogonalize the localized GVB orbitals; (2) evaluate all integrals in terms of these localized orbitals and apply the  $\delta J$  correction to each one-center self-Coulomb integral; (3) transform these orbitals and integrals back to the GVB natural orbitals for use in configuration-interaction (CI) calculation; (4) recalculate the usual GVB-RCI (where R signifies restricted) wave function [two configurations for  $H_2$ , fourteen spatial configurations (twenty spin eigenfunctions) for  $N_2$ , 365 spatial configurations (1516 spin eigenfunctions) for  $Cr_2$  and  $Mo_2$ ] with use of the modified integrals; (5) in calculating the CI wave function of (4), the corrected integrals are used only

for bond pairs in which either the bonding or antibonding GVB natural orbital is doubly occupied [as in the GVB-PP (where PP signifies perfect pairing) wave function] since only in this case is there static ionic character in the wave function.

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<sup>11</sup>All ionization potentials are from C. E. Moore, *Atomic Energy Levels*, U. S. National Bureau of Standards Circular No. 467 (U.S. GPO, Washington, D.C., 1971).

<sup>12</sup>A. Lofthus and P. H. Krupenie, *J. Phys. Chem. Ref. Data* **6**, 113 (1977).

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<sup>16</sup>B. Delley, A. J. Freeman, and D. E. Ellis, *Phys. Rev. Lett.* **50**, 488 (1983); J. Bernholc and N. A. W. Holzwarth, *Phys. Rev. Lett.* **50**, 1451 (1983); R. P. Messmer, *J. Vac. Sci. Technol. A* **2**, 899 (1984); N. A. Baykara, B. N. McMaster, and D. R. Salahub, *Mol. Phys.* (to be published).

<sup>17</sup>For example, T. Takada and K. Freed, *J. Chem. Phys.* **80**, 3253 (1984).