

## Nature of Mo-Mo and Cr-Cr Multiple Bonds: A Challenge for the Local-Density Approximation

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The full potential curves for Mo<sub>2</sub> (and Cr<sub>2</sub>) have been examined by using highly correlated wave functions. A competition is found between 5s-5s bonding and 4d-4d bonding, so that the lower states lead to two minima, with the inner minimum involving  $d\sigma$ ,  $d\pi$ , and  $d\delta$  bonds. The results disagree dramatically with those from local-density calculations, and the present analysis suggests that this approximation (in its current formulation) is unsuitable for describing multiple bonds in transition-metal systems.

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There remains a great deal of uncertainty concerning the nature of metal-metal bonding, particularly in transition metals. Questions involve the relative role of  $s$ ,  $p$ , and  $d$  components and the possibility of  $d\pi$  and  $d\delta$  bonding. Simple systems for which it should be possible to unambiguously settle such questions are the Cr<sub>2</sub> and Mo<sub>2</sub> diatomic molecules. However, despite numerous experimental and theoretical studies, there remains considerable controversy. Ground states have been suggested to be  $1^2\ ^1\Sigma_u^+$ ,  $3\Sigma_g^-$ , and  $1\Sigma_g^+$ , and the description of bonding has ranged from a single  $s$ - $s$  bond<sup>2</sup> to a quadruple bond or a sextuple bond.<sup>1,3</sup> Of particular concern here is that local-density formalisms thought to be quite adequate for describing transition-metal solids<sup>4,5</sup> are known to fail<sup>1</sup> in accounting for the bonding in Cr<sub>2</sub>.

A major difficulty with the theoretical study of such systems is the extremely large effect of electron correlations (many-body effects), as indicated in Fig. 1(a). Here we see that the Hartree-Fock (HF) wave function of the sextuple-bonded state ( $1\Sigma_g^+$ ) of Mo<sub>2</sub> leads to an energy over 9 eV *higher* than the energy of two HF atoms. Indeed, the unrestricted HF wave function (UHF), which necessarily goes to the proper limit as  $R \rightarrow \infty$ , totally fails in accounting for the Mo-Mo bond, leading to an energy that is 3.5 eV *unbound* at the experimental bond distance. The problems with the (closed-shell) HF wave function are its inability to describe the high-spin coupling required in the  $d^5$  configuration of separated atoms and its inability to describe weakly overlapping orbitals on different centers. The UHF wave function allows high-spin coupling of the electrons at each atom (but only at the expense of building in an artificial net spin density at each atom). This wave function fails in that it cannot allow

strong bonding interactions of the orbitals on different centers (without giving up the favorable spin coupling within each atom). Since these determinantal wave functions form the basis of all current local-density or local-spin-density calculations, we feel that such calculations on Mo, W, Cr, and other transition metals having multiple unpaired  $d$  electrons are quite suspect. Indeed, the cohesive energies calculated with use of local-density methods in transition-metal solids such as Mo use as the reference atomic energy an energy far above the ground-state energy of the atom.<sup>4,5</sup> This is analogous to calculating the bond energy for Mo<sub>2</sub> by using the well depth in the HF description [upper curve in Fig. 1(a)]. Because of the large atomic spin coupling energy, it is likely that local-spin-density calculations for a metal such as Mo would exhibit almost no cohesive energy and very bad geometries [analogous to the UHF curve in Fig. 1(a)]. Since determinantal wave functions are the basis for essentially all calculations on transition-metal solids, one must be concerned for the validity of our understanding of these systems. Whatever method is developed to solve this problem it should be capable of describing the bonding between transition metals. We will describe below the simplest wave function that currently can describe the bonding in Mo<sub>2</sub>. The challenge is to find a way to extend the essence of this method to infinite systems.

In order to provide a proper description of Mo<sub>2</sub>, we have developed a new method [generalized valence bond (GVB)-van der Waals (vdw)] that includes all possible ways of coupling the twelve valence electrons of Mo<sub>2</sub> plus the correlations responsible for van der Waals interactions.<sup>6</sup> Thus this wave function dissociates properly and contains the dominant electron correlation effects.

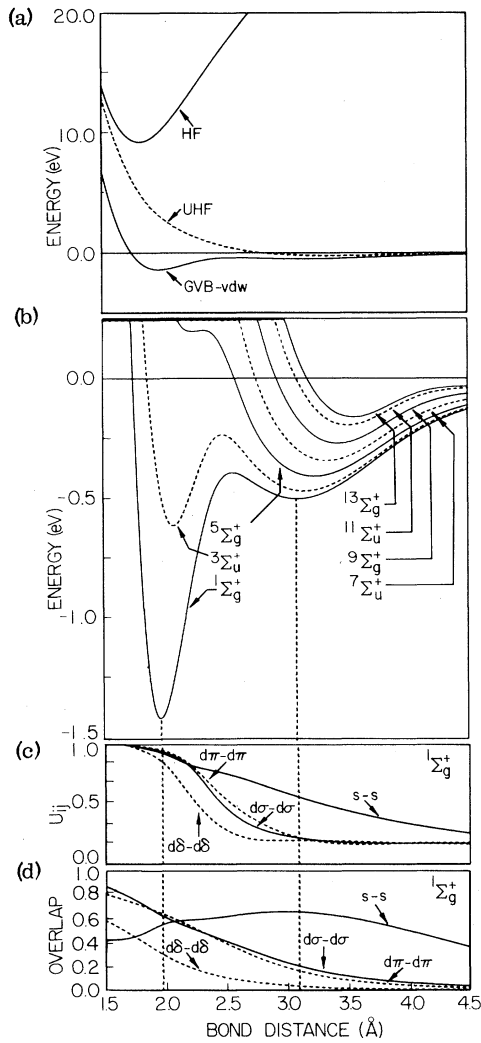


FIG. 1. (a) Comparison of potential curves for  $\text{Mo}_2$  from our ground-state wave function (GVB-vdw) and the corresponding HF and UHF wave functions. (b) The potential curves (GVB-vdw) for  $\text{Mo}_2$ . (c) The spin coupling ( $U_{ij}$ ) for each bond of  $\text{Mo}_2$ . (d) The overlap between bonding orbitals of  $\text{Mo}_2$ .

For the  $1^1\Sigma_g^+$  state, this wave function leads to 26 512 Slater determinants involving eighteen valence molecular orbitals where the orbitals are optimized self-consistently for the full 26 512-determinant wave function<sup>2,6,7</sup> (a most extensive *ab initio* wave function).

For  $\text{Mo}_2$  the calculated bond distance of 1.97 Å for the ground state ( $1^1\Sigma_g^+$ ) is in good agreement with the experimental value<sup>8</sup> of 1.93 Å, and the calculated vibrational frequency of 455  $\text{cm}^{-1}$  is in reasonable agreement with the experimental value<sup>8</sup> of 477  $\text{cm}^{-1}$ .

The ground state of the Mo atom has the va-

lence configuration  $(4d)^5(5s)^1$  with spin  $S=3$ . The states of  $\text{Mo}_2$  that correlate with two ground-state Mo atoms have total spins  $S=0, 1, 2, 3, 4, 5,$  and 6 (one state for each spin). These states at larger internuclear separation have an energy spectrum of the form  $E_s = E_0 - JS(S+1)$ , where  $J < 0$ , leading to a singlet ground state ( $1^1\Sigma_g^+$ ) (note that  $J \rightarrow 0$  as  $R \rightarrow \infty$ ).

For  $\text{Cr}_2$  we find that the ground state of the molecule is of this form with a spectrum of excited states well described by a single  $J$  and leading to a bond distance of  $R_e = 3.06$  Å, a vibrational frequency of  $\omega_e = 110$   $\text{cm}^{-1}$ , and a bond energy of  $D_e = 0.35$  eV. The Heisenberg coupling constant  $J$  is accurately exponential over the range of bonding, leading to  $J = ae^{-bR}$ , with  $a = -3040$   $\text{cm}^{-1}$  and  $b = 1.14$  Å<sup>-1</sup>.

Our results strongly disagree with density functional theory<sup>1</sup> which gives only one bound state ( $1^3\Sigma_g^+$  with a bond energy of 0.2 eV) for  $\text{Cr}_2$  and finds our ground state ( $1^1\Sigma_g^+$ ) unbound by over 1.9 eV. This disagreement illustrates that even a qualitative description of this system requires a proper treatment of spin coupling and casts doubt on the efficacy of the local (spin) density approximation in calculations on transition-metal systems.

For  $\text{Mo}_2$  we also find a potential well at  $R_e = 3.09$  Å having  $\omega_e = 80$   $\text{cm}^{-1}$  and  $D_e = 0.49$  eV. In this region there is significant  $5s-5s$  overlap but little  $4d-4d$  overlap, so that the bonding is dominated by the  $5s$  orbitals. However, a unique feature of the  $\text{Mo}_2$  potential curves [see Fig. 1(b)] is the hump and inner minimum leading to a double well in the ground state ( $1^1\Sigma_g^+$ ) and some of the lower lying states. Next we will consider the origin of this double well.

From our wave functions we can evaluate the spin coupling between electrons by using the spin operator  $-\frac{1}{2} - 2(\hat{s}_i \cdot \hat{s}_j)$ , whose expectation value<sup>9</sup>  $U_{ij}$  ranges from  $-1$  for triplet spin coupling to  $+1$  for singlet spin coupling. The optimal coupling between electrons in orthogonal orbitals is  $U_{ij} = -1$  (triplet), whereas the optimal coupling between bonding electrons is  $U_{ij} = +1$  (singlet). For the Mo atom, the optimal coupling among the six valence electrons is  $U_{ij} = -1$ , giving  $S=3$ . For  $\text{Mo}_2$ , coupling two  $S=3$  atoms into an overall singlet state gives the optimal intra-atomic energy but results in  $U_{ij} = +\frac{1}{6}$  between bonding electrons, yielding only about  $\frac{1}{6}$  the maximal bond energy. Alternatively, coupling the electrons within each bond as  $U_{ij} = +1$  gives maximal bonding but results in  $U_{ij} = -\frac{1}{2}$  between electrons in differ-

ent bonds, yielding a great loss in intra-atomic energy (a loss of 7 eV for  $\text{Mo}_2$ ).

In Fig. 1(c) we plot the spin coupling ( $U_{ij}$ ) for each bond as a function of  $R$ . Here we see that at the outer minimum  $U_{ss}$  has increased from  $\frac{1}{6}$  to 0.55, but each  $U_{dd}$  is still  $\sim 0.2$ . This occurs because there is bonding between the 5s orbitals of the Mo atoms but no bonding between the  $d$  orbitals. Bonding between the  $d$  orbitals does not occur at larger  $R$  because the  $d$ - $d$  overlaps are too small for the resulting bonds to compensate for the concomitant loss in intra-atomic energy.

In Fig. 1(d) we plot orbital overlaps as a function of  $R$ . Here we see that the outer minimum of the singlet potential corresponds to the optimum  $R$  for  $s$ - $s$  bonding. As  $R$  is decreased below 3.09 Å, the energy increases until the atoms get close enough for  $d$ - $d$  overlaps to provide sufficient bonding to compensate for the loss in intra-atomic energy. This occurs by 2.5 Å, resulting in a sharp drop in the potential curve and a minimum (at 1.97 Å) characterized by strong bonding of all  $d$  orbitals. Thus, at  $R = 1.93$  Å, we find  $U_{\sigma\sigma} = 0.95$ ,  $U_{\pi\pi} = 0.96$ ,  $U_{\delta\delta} = 0.88$ , and  $U_{ss} = 0.94$ . This indicates that all five  $d$  orbitals on each center strongly participate in bonding. Particularly noteworthy here is the value of  $U_{\delta\delta}$ . With no  $\delta$  bonding, the two  $\delta$  orbitals on a center would be high-spin coupled ( $U_{ij} = -1$ ), leading to  $U_{\delta\delta} = +\frac{1}{2}$  for  $\delta$  orbitals on opposite centers (since all other bonds are coupled  $U_{ij} = +1$ ). Since  $U_{\delta\delta} = 0.88$ , there is clearly *strong bonding between  $\delta$  orbitals!* The  $U$ 's and especially the orbital overlaps suggest that the  $s$ - $s$  bond is not as strong as the  $d\sigma$ - $d\sigma$  bond at  $R_e$ . Our wave function shows very little  $s$ - $d\sigma$  hybridization (less than 10% at  $R_e$ ), indicating that  $s$ - $d\sigma$  bonding is much less important than  $d\sigma$ - $d\sigma$  (or  $s$ - $s$ ).

In summary, *the ground state of  $\text{Mo}_2$  has a double-well potential curve where (1) the outer minimum has an  $s$ - $s$  bond, but with a high-spin  $d^5$  configuration on each atom, and (2) the inner minimum has  $d\sigma$ - $d\sigma$ ,  $d\pi$ - $d\pi$ , and  $d\delta$ - $d\delta$  bonding.* A hump occurs between these two points because  $R$  must be decreased below the optimum for  $s$ - $s$  bonding before  $d$ - $d$  overlaps are sufficient to start making  $d$ - $d$  bonds. For  $\text{Cr}_2$  we find an outer minimum (at 3.1 Å) similar to the outer minimum for  $\text{Mo}_2$ ; however, at smaller  $R$ , the  $d$ - $d$  overlaps for  $\text{Cr}_2$  are not large enough to compensate for various repulsive interactions so that no second bound minimum is found. These results suggest that at  $R_e$ ,  $\text{Mo}_2$  has a quintuple bond (one  $\sigma$ , two  $\pi$ , and two  $\delta$ ) with the  $s$ - $s$  interaction be-

ing somewhat repulsive. This result disagrees with other interpretations<sup>3</sup> which conclude that the  $s$ - $s$  interaction decreases the bond distance but that the  $\delta$ - $\delta$  interactions have little effect. However, our result supports the interpretation<sup>4,5</sup> that in 4d transition-metal solids the valence  $d$  electrons are attractive while the valence  $s$  electrons are repulsive.

The  $S = 1, 2, 3, 4, 5,$  and 6 states also lead to outer minima (at 3.15 Å for  $^3\Sigma_u^+$ ) involving 5s-5s bonds similar to that in  $^1\Sigma_g^+$ . However, at small  $R$ , these higher-spin states have successively fewer bond pairs and hence only the  $^3\Sigma_u^+$  state has a pronounced inner minimum ( $R_e = 2.07$  Å,  $\omega_e = 325$   $\text{cm}^{-1}$ , and  $D_e = 0.60$  eV). In this case we find (at 1.93 Å)  $U_{\sigma\sigma} = 0.93$ ,  $U_{\pi\pi} = 0.94$ ,  $U_{\delta\delta} = 0.49$ , and  $U_{ss} = -0.10$ , so that the  $d\sigma$  and  $d\pi$  bonding is similar to  $^1\Sigma_g^+$  but the  $d\delta$  bonds are weak and the 5s pair is slightly antibonding.

For Mo-Mo systems with ligands on the Mo, the 5s orbitals are generally destabilized so that the existence of the outer minimum is less likely. However, since the inner minimum of  $\text{Mo}_2$  is dominated by  $d$ - $d$  interactions, the character of this minimum should correspond closely with the interaction of Mo-Mo systems having ligands on the Mo. This appears to be the case since systems thought to have Mo-Mo quadruple bonds lead to bond distances<sup>10</sup> of  $2.1 \pm 0.05$  Å, which is consistent with the 1.97 Å we find for the quintuple bond in  $\text{Mo}_2$ .

The bond energy of  $\text{Mo}_2$  has been determined experimentally<sup>11</sup> by using a Knudsen cell and a mass spectrometer to determine the relative concentrations of  $\text{Mo}_2$  and Mo as a function of  $T$ . Thus, to obtain a bond energy it is necessary to estimate the partition function. The experiments were interpreted in terms of a single  $^1\Sigma_g^+$  state for  $\text{Mo}_2$ , leading to  $D_0 = 4.2 \pm 0.2$  eV (Ref. 11) (the calculated bond energy is  $D_e^{\text{calc}} = 1.41$  eV). Since there are a number of bound states of  $\text{Mo}_2$ , the partition function may change significantly, leading to a modified experimental bond energy. Other potential experimental problems involve the possibility of nonhydrodynamic (supersonic) flow (which would lead to a lower effective temperature than in the oven) or kinetically limited flow (lack of thermodynamic equilibrium).<sup>12</sup>

These results on  $\text{Mo}_2$  suggest that at equilibrium the  $d$ - $d$  interactions are bonding while the  $s$ - $s$  interactions are repulsive. They also show the importance of  $\delta$ - $\delta$  bonds for transition metals. For  $\text{Mo}_2$  the use of single determinantal wave functions (HF or UHF) yields a totally inadequate

description, suggesting that a modified framework must be used to provide a proper description of transition-metal solids. Since a key aspect of the bonding involves the  $U_{ij}$  or  $S_i \cdot S_j$  terms, perhaps the local-density formulations can be modified to explicitly include such terms (e.g.,  $\sum_{i,j} J_{ij} S_i \cdot S_j$ ) where the  $J_{ij}(R)$  are obtained from molecular calculations.

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<sup>6</sup>The van der Waals (vdw) configurations allow simultaneous  $s \rightarrow p\sigma$  or  $p\pi$  excitations on each center while including all configurations corresponding to appropriate  $d^5$  on each atom. The basis set consists of a valence (i.e.,  $4d, 5s, 5p$ ) double-zeta basis for Mo to which we add a set of  $f$  basis functions on each Mo optimized for the GVB-PP wave function at  $R = 1.93 \text{ \AA}$  ( $\alpha_{\text{opt}} = 0.45$ ).

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## Hysteresis in Cyclotron Resonance Based on Weak Relativistic-Mass Effects of the Electron

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The cyclotron resonance is considered upon action of strong electromagnetic quasisresonant wave. It is shown that even a very weak relativistic ( $\beta^2 \ll 1$ ) mass effect of the electron can result in large hysteretic jumps of its steady-state kinetic energy, if the wave intensity or frequency is varied.

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This paper is basically to attract attention to the fact that even a very weak relativistic ( $\beta^2 \ll 1$ ) mass effect can result in large nonlinear effects in such a very well studied phenomenon as free-electron cyclotron resonance. The proposed effect is important because it suggests for the first time, to our best knowledge, bistable interaction of an electromagnetic wave with the simplest microscopic physical object. This differs fundamentally from all kinds of optical bistability<sup>1-3</sup> presently known, which so far has always been based on macroscopic nonlinear properties of the media. Nonlinear change in macroscopic

susceptibility under action of the strong EM wave provides dramatic change in the optical condition of propagation of this wave under various special circumstances (e.g., in nonlinear Fabry-Perot resonators<sup>1</sup>; at nonlinear interfaces<sup>2</sup>; or in counterpropagating beams of light,<sup>3</sup> interacting with each other) which, in turn, leads again to the change in the susceptibility. This so-called optical feedback in nonlinear macrosystems results in the existence of multistable (in particular, bistable) steady states. No such optical feedback exists in the case considered in this paper.