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_2 (and Cr_2) 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.

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_2 and Mo_2 diatomic molecules. However, despite numerous experimental and theoretical studies, there remains considerable controversy. Ground states have been suggested to be[1,2] $^{11}\Sigma_u^+$, $^3\Sigma_g^-$, and $^1\Sigma_g^+$, and the description of bonding has ranged from a single s–s bond[2] to a quadruple bond or a sextuple bond.[1,3] Of particular concern here is that local-density formalisms thought to be quite adequate for describing transition-metal solids[4,5] are known to fail[1] in accounting for the bonding in Cr_2.

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_2 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 $R \to \infty$, 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 fee 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.[4,5] This is analogous to calculating the bond energy for Mo_2 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_2. 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_2, 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_2 plus the correlations responsible for van der Waals interactions.[6] Thus this wave function dissociates properly and contains the dominant electron correlation effects.
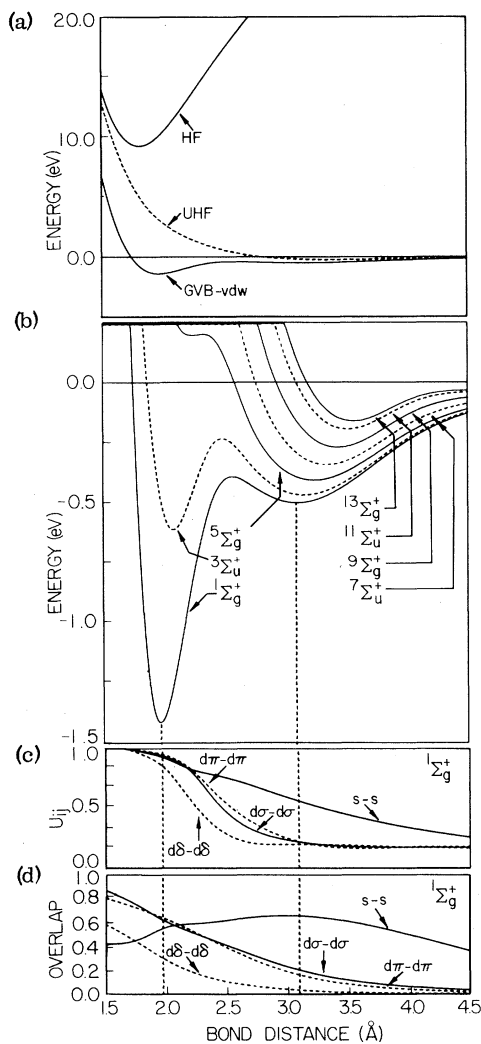
FIG. 1. (a) Comparison of potential curves for Mo_2 from our ground-state wave function (GVB-vdw) and the corresponding HF and UHF wave functions. (b) The potential curves (GVB-vdw) for Mo_2. (c) The spin coupling (U_{ij}) for each bond of Mo_2. (d) The overlap between bonding orbitals of Mo_2.

For the $^1\Sigma_g{}^+$ 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[2,6,7] (a most extensive *ab initio* wave function).

For Mo_2 the calculated bond distance of 1.97 Å for the ground state ($^1\Sigma_g{}^+$) is in good agreement with the experimental value[8] of 1.93 Å, and the calculated vibrational frequency of 455 cm^{-1} is in reasonable agreement with the experimental value[8] of 477 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 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 ($^1\Sigma_g{}^+$) (note that $J \rightarrow 0$ as $R \rightarrow \infty$).

For 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 $R_e = 3.0\underline{6}$ Å, a vibrational frequency of $\omega_e = 110$ cm^{-1}, and a bond energy of $D_e = 0.3\underline{5}$ eV. The Heisenberg coupling constant J is accurately exponential over the range of bonding, leading to $J = ae^{-bR}$, with $a = -3040$ cm^{-1} and $b = 1.14$ Å^{-1}.

Our results strongly disagree with density functional theory[1] which gives only one bound state ($^{13}\Sigma_g{}^+$ with a bond energy of 0.2 eV) for Cr_2 and finds our ground state ($^1\Sigma_g{}^+$) 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 Mo_2 we also find a potential well at $R_e = 3.09$ Å having $\omega_e = 80$ 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 Mo_2 potential curves [see Fig. 1(b)] is the hump and inner minimum leading to a double well in the ground state ($^1\Sigma_g{}^+$) 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[9] 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 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 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 ~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 δ bonding, the two δ orbitals on a center would be high-spin coupled $(U_{ij} = -1)$, leading to $U_{\delta\delta} = +\frac{1}{2}$ for δ 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 δ 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 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 Cr_2 we find an outer minimum (at 3.1 Å) similar to the outer minimum for Mo_2; however, at smaller R, the d-d overlaps for 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, Mo_2 has a quintuple bond (one σ, two π, and two δ) with the s-s interaction be-

ing somewhat repulsive. This result disagrees with other interpretations[3] which conclude that the s-s interaction decreases the bond distance but that the δ-δ interactions have little effect. However, our result supports the interpretation[4,5] 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, $\omega_e = 325$ 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 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[10] of 2.1 ± 0.05 Å, which is consistent with the 1.97 Å we find for the quintuple bond in Mo_2.

The bond energy of Mo_2 has been determined experimentally[11] by using a Knudsen cell and a mass spectrometer to determine the relative concentrations of 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 Mo_2, leading to $D_0 = 4.2 \pm 0.2$ eV (Ref. 11) (the calculated bond energy is $D_e^{calc} = 1.41$ eV). Since there are a number of bound states of 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).[12]

These results on 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 δ-δ bonds for transition metals. For Mo_2 the use of single determinantal wave functions (HF or UHF) yields a totally inadequate

description, suggesting that a modified frame-
work must be used to provide a proper descrip-
tion of transition-metal solids. Since a key as-
pect 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 ob-
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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 quasires-
onant wave. It is shown that even a very weak relativistic ($\beta^2 \ll 1$) mass effect of the elec-
tron can result in large hysteretic jumps of its steady-state kinetic energy, if the wave in-
tensity 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 ef-
fect 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 funda-
mentally from all kinds of optical bistability[1-3]
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 vari-
ous special circumstances (e.g., in nonlinear
Fabry-Perot resonators[1]; at nonlinear inter-
faces[2]; or in counterpropagating beams of light,[3]
interacting with each other) which, in turn, leads
again to the change in the susceptibility. This
so-called optical feedback in nonlinear macro-
systems results in the existence of multistable
(in particular, bistable) steady states. No such
optical feedback exists in the case considered in
this paper.