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Determination of the electronic configuration of the ground state of iron dimer through analysis of ^{57m}Fe Mössbauer data

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The hyperfine properties of ^{57m}Fe in the diatomic iron molecule have been analyzed using the self-consistent-field unrestricted Hartree-Fock procedure. The ^{57m}Fe quadrupole interaction and isomer shift strongly support $^3\Sigma_g$ as the ground state for the Fe_2 molecule, with $^7\Sigma_g$ leading to less satisfactory agreement with experimental data but better than for other possible states. The analysis of the magnetic hyperfine-field tensor also appears to provide support for the $^3\Sigma_g$ model through agreement with the evidence from Mössbauer studies that the direction of the maximum component is perpendicular to the internuclear axis, the direction of the maximum component of the electric-field-gradient tensor. The magnitudes of the hyperfine-field components are however underestimated by a factor of about 2 compared to experiment. Possible sources that could contribute to this departure are discussed.

I. INTRODUCTION

The electronic properties of atoms and molecules in nearly free configurations have been experimentally studied[1] in the literature by rare-gas matrix isolation techniques. Application[2] of this technique in Mössbauer experiments has provided the ^{57m}Fe quadrupole coupling constants e^2qQ for a number of systems. In a recent theoretical analysis[3] of the Mössbauer data[4] on $FeCl_2$ and $FeBr_2$ trapped in argon matrix, involving the evaluation of the electric field gradient (EFG) at the ^{57m}Fe nucleus using electronic wave functions obtained by the first-principle unrestricted Hartree-Fock (UHF) procedure, the quadrupole moment of ^{57m}Fe was determined to be 0.082 b, substantially smaller than the values 0.16 to 0.28 b that were used before this work. Subsequently, this value for $Q(^{57m}\mathrm{Fe})$ has been supported by analysis[5] of ^{57m}Fe quadrupole interaction data in transition-metal alloys and through a combination[6,7] of perturbed angular correlation and Mössbauer measurements of ^{54}Fe and ^{57m}Fe on the same compounds which provided the ratio R of the quadrupole moments of the two isotopes. Since the quadrupole moment of the heavily distorted nucleus ^{54}Fe is very well predicted[8] by nuclear-structure theory, the measurement of R provides a value of $Q(^{57m}\mathrm{Fe})$, which has been found[6,7] to be 0.080 ± 0.007 b very close to the value[3] from $FeCl_2$ and $FeBr_2$ data.

Earlier theoretical investigations of the diatomic transition-metal molecules concerning their ground-state configuration have led to somewhat controversial conclusions. The visible absorption spectra of a number of these molecules in rare-gas solid matrices have been interpreted[9] as indicative of a $^1\Sigma_g$ ground state in the majority of cases, while for some of them, including Ni_2, a triplet ground state, $^3\Sigma_g$ is suggested. Extended Hückel[10] calculations on these molecules (aimed at explaining the dissociation energies, ionization potentials, and stretching frequencies) have led[11] to ground states in agreement with those derived from visible absorption spectroscopic data,[12] including a $^3\Sigma_g$ state for Ni_2. For Fe_2, where the characterization of the ground state from optical data is not available, the extended Hückel calculations[11] suggest a $^3\Sigma_g$ state. Finally, a generalized valence-bond calculation[13] on the diatomic molecules Mo_2 and Cr_2, including configuration interaction to incorporate correlation effects, suggests a $^1\Sigma_g$ state for both molecules. Thus, in general, all these investigations support low spin states for diatomic transition metal systems. However, calculations[14–16] based on the local- (spin-) density approximation[17] to the exchange interaction between electrons involving the Slater-type[18] one-electron approximation to the exchange, have led to ground states with high spin for these diatomic molecules. Thus a density-functional calculation[14] of the energy has led to a $^7\Delta_u$ state for Fe_2 dimer. On the other hand, the analysis[15] of Mössbauer data by a discrete-variational-method (DVM)—$X\alpha$ calculation has supported a $^7\Pi_u$ state while a similar investigation[16] by the self-consistent-field (SCF)—$X\alpha$—scattered wave procedure suggests $^7\Sigma_g$ or $^9\Sigma_g$ states.

The motivation for the present investigation is to examine, using the UHF procedure without any approximation to the exchange interaction, which molecular state best explains the available ^{57m}Fe nuclear quadrupole, magnetic hyperfine, and isomer shift data[19] in an attempt to shed further light on the question of the proper spin state for the Fe_2 molecule. Section II presents a brief description of the procedures we have employed for the electronic structure calculations and the evaluation of the quadrupole coupling constant, hyperfine field, and isomer shift for ^{57m}Fe. Section III deals with the results and discussion and Sec. IV the conclusions from our work.

II. PROCEDURE

A. Method for electronic structure calculations

In our calculations we have used UHF molecular wave functions obtained by the POLYATOM system[3,20–22] of molecular programs and the analytic expansion method for the molecular orbitals. With this method, the UHF molecular orbitals (MO)ψ_μ are expressed as a linear combination of basis functions χ_i as in

$$\psi_\mu = \sum_i A_{\mu i}\chi_i \,, \tag{1}$$

where $A_{\mu i}$ are the MO expansion coefficients. The basis functions χ_i which are centered at the nuclear sites in the molecules are expressed as contractions of primitive Gaussian functions in the following way:[20,22]

$$\chi_i = \sum_\kappa c_{i\kappa}\eta_\kappa x^{l_i} y^{m_i} z^{n_i} e^{-\zeta_\kappa r^2}, \quad l_i + m_i + n_i = L_i \,, \tag{2}$$

where $c_{i\kappa}$ are the contraction coefficients for the ith function, ζ_κ and η_κ correspond to the exponents and normalization factor, respectively, for the normalized Gaussian functions, while L_i is the orbital-angular-momentum quantum number for the ith basis function.

The advantage of using Gaussian basis functions and the need for using "contracted" Gaussian type of orbitals instead of individual Gaussian functions, as a compromise between accuracy and practicability, have been discussed elsewhere.[22] Within this procedure, the basis set we have used for each of the iron sites consists of nine contracted s functions composed of fourteen primitive Gaussians, four contracted p functions composed of nine primitive Gaussians, and three contracted d functions composed of five primitive Gaussians. The exponents and the contraction coefficients for the primitive Gaussians are available in the literature.[23]

The UHF method includes the exchange interaction between all electrons, core and valence, without any approximation. This latter point is very important since it is well known that hyperfine fields, especially, are very sensitive[24] to exchange core polarization effects. This effect arises[25] from the influence of the exchange between the unpaired spin electron and the electron in a paired spin state with spin parallel to the former, which makes the wave functions of the two paired spin states different from one another. Attempts[26] to approximate the true exchange interaction between electrons with local-density potentials[18,27] have been found to lead to serious problems for the exchange core polarization effect, even in the case of alkali-metal atoms. A possible reason for this, suggested in the literature,[28] is that the statistical exchange approximation on which the density-functional approach is based does not hold near the nucleus where the electron density varies rather drastically. The local density approximation is more successful with properties related to energy involving averaging over all space, rather than a particular region of space as in the case for hyperfine parameters.

B. Hyperfine parameters

The three hyperfine parameters which can be obtained experimentally from Mössbauer spectroscopy are the product of a nuclear factor with an electronic factor. The isomer shift is the monopole Coulombic interaction between the electronic charge density at the nucleus $\rho(0)$ and the nuclear charge. For similar nuclei in two different compounds, the energy shift between the Mössbauer spectra, which is related to the difference in electronic charge densities at the nucleus in the two systems, is given by[29]

$$\begin{aligned}\delta\varepsilon = \varepsilon_1 - \varepsilon_2 = 15.6\times 10^{-26} Z A^{2/3} E_\gamma^{-1} S'(Z)\\ \times[\rho_1(0)-\rho_2(0)]\delta R/R \,.\end{aligned} \tag{3}$$

In this equation $\delta R/R$ is the fractional change in the nuclear charge radius during the γ-ray transition, Z and A being the nuclear charge and mass of the nucleus, and E_γ is the γ-ray energy in keV. The electronic charge densities at the nucleus are calculated from nonrelativistic molecular wave functions and a correction factor $S'(Z)$ is applied to incorporate relativistic effects. In our present work, we shall follow the conventional practice in the literature of using a relation of the form

$$\delta\varepsilon = \alpha[\rho_1(0)-\rho_2(0)] \,, \tag{4}$$

where α incorporates all the nuclear factors in Eq. (3). This factor, referred to as the isomer-shift calibration constant, is obtained[30,31] from comparison of the experimentally observed isomer shifts and calculated nonrelativistic density differences in iron compounds from first-principle Hartree-Fock investigations. As in our recent work[22] on the isomer shifts in iron dihalides, for the reasons discussed there, we have used the value[31] of $\alpha = -0.3 \pm 0.03$ mm/sec $e\,a_0^{-3}$ available in the literature.

The nuclear quadrupole interaction between the nuclear quadrupole moment and the electric field gradient at the site of the nucleus, produced by the anisotropy of the electronic charge distribution, gives rise to a quadrupole splitting of the nuclear energy levels. For the case of the metastable state ^{57m}Fe of the iron nucleus with nuclear spin $I=\frac{3}{2}$ in an axially symmetric environment this splitting is given by[32]

$$\Delta E_Q = \tfrac{1}{2}e^2 qQ \,, \tag{5}$$

where Q is the quadrupole moment of ^{57m}Fe nucleus in the excited state (nuclear spin $\frac{3}{2}$) of the 14.4-keV transition, and $eq \equiv V_{z'z'} = (\delta^2 V/\delta z'^2)_0$ is the maximum component of the electric field gradient (EFG) in the principal axis system. There are two contributions to the EFG, from the nuclear charges (the charge on the nucleus of the other iron atom in the iron dimer) and from the electronic charge distribution. Thus,

$$\begin{aligned} q = \sum Z_N \left[\frac{3\cos^2\theta_N - 1}{r_N^3}\right] \\ - \sum_\mu \left[\left\langle \psi_{\mu\uparrow}\left|\frac{3\cos^2\theta - 1}{r^3}\right|\psi_{\mu\uparrow}\right\rangle \right. \\ \left. + \left\langle \psi_{\mu\downarrow}\left|\frac{3\cos^2\theta - 1}{r^3}\right|\psi_{\mu\downarrow}\right\rangle\right] \end{aligned} \tag{6}$$

the subscript N running over all nuclear charges and μ over all occupied molecular orbitals, respectively. Since all electrons in the molecule, including the core electrons on the atoms are included in the second term, there is no necessity for any Sternheimer antishielding factors,[16,33] the antishielding effects being directly included through the distortion of the core orbitals from spherical symmetry.

The magnetic hyperfine splitting of the nuclear levels originates from the interaction of the magnetic dipole moment of the nucleus with the magnetic hyperfine field produced by the electrons surrounding the nucleus under study. The major contributor to the hyperfine field in the iron dimer, as in transition-metal compounds[25,34] and ferromagnetic metals,[35] is expected to be the contact term arising primarily from exchange core polarization effects. In the direction of the majority spin, this contribution to the hyperfine field is given by

$$H_{\text{hf}}^{\text{cont}}=\frac{8\pi}{3}\mu_B a_0^{-3}\sum_{\mu}[\,|\psi_{\mu\uparrow}(0)|^2-|\psi_{\mu\downarrow}(0)|^2] \qquad (7)$$

the conversion factor $(8\pi/3)\mu_B a_0^{-3}$ being 524.2 kG.

The hyperfine field due to the dipolar term is however expected to be sizable in the Fe_2 molecule, because of the substantial axial distortion in the electron distribution in the neighborhood of the nucleus produced by the bonding between the atoms. The dipolar contribution in the direction of the internuclear axis is given by

$$H_{\text{hf}}^{\text{dip}}=\mu_B a_0^{-3}\left[\sum_{\mu}\left\langle\psi_{\mu\uparrow}\left|\frac{3\cos^2\theta-1}{r^3}\right|\psi_{\mu\uparrow}\right\rangle -\left\langle\psi_{\mu\downarrow}\left|\frac{3\cos^2\theta-1}{r^3}\right|\psi_{\mu\downarrow}\right\rangle\right] \qquad (8)$$

the conversion factor $\mu_B a_0^{-3}$ being 62.6 kG.

All three hyperfine interactions have been studied[19] by Mössbauer spectroscopy for Fe_2 dimer in rare-gas solids leading to quite accurate results. The experimental results that we shall use for comparison with theory are the isomer shift with respect to iron metal, $\delta\varepsilon=-0.14\pm0.02$ mm/sec, the quadrupole splitting $\Delta E_Q=-4.05\pm0.04$ mm/sec and the maximum component of the hyperfine field at the site of the ^{57m}Fe nucleus of $|600|\pm15$ kG.

III. RESULTS AND DISCUSSION

The results for the field gradient for a number of multiplet states that we have studied using Hartree-Fock procedure are presented in Table I. To study the sensitiveness of the results with respect to the bond length, we have calculated the field gradient for two bond lengths, 2.0 and 1.87 Å, for the two multiplet states $^3\Sigma_g$ and $^7\Sigma_g$. These two distances were chosen because extended x-ray absorption fine structure (EXAFS) measurements for Fe_2 trapped in solid argon have led[36] to a bond length of (1.87 ± 0.13) Å, the distance 2.0 Å being the maximum value of this bond length within the experimental range of error. For the rest of the multiplet states, the calculation was performed with a bond distance of 1.87 Å. To provide some insight into the origin of the field gradients we have listed separately in columns 3, 4, and 5 the contributions to the field gradient from *s*-like, *p*-like, and *d*-like orbitals, this characterization being made according to the largest angular components in the molecular orbitals. The sixth column presents the net electronic contributions and is followed by the contributions from the nuclear charge on the other iron atom. The total field gradient is given in the ninth column which is converted to the quadrupole splitting in the Mössbauer spectra [Eq. (5)] in the last column. The value of $Q(^{57m}\text{Fe})$ used in deriving the quadrupole splitting from the EFG is the recent one of 0.082 b. The source[3] of this value and supporting evidences[5,6] for it have already been cited in the Introduction. A recent covalency calculation[37] in α-Fe_2O_3 by the multiple scattering $X\alpha$ procedure,[38] which uses a statistical exchange approximation to the Hartree-Fock approach, has led to a value of 0.11 b for $Q(^{57m}\text{Fe})$. This value is much closer to the recent value[3] than the earlier ones in the range of 0.16 to 0.28 b used in the literature.

From Table I, the *d*-like contribution is seen to be the dominant one followed by the *s* like and then the *p* like. One can understand this trend as follows. The *d* shell is incomplete in the free atom, already having an anisotropy around the nucleus. This anisotropy is further accentuated by molecular orbital formation. The 4*s* orbitals on the atoms by themselves cannot produce any EFG. However, their mixing with the *d* orbitals in the molecule can lead to anisotropy resulting in significant contribution to the

TABLE I. Electric field gradient contributions in Fe_2 molecule for various molecular states. All contributions are given in atomic units (ea_0^{-3}).

	Bond		Molecular orbitals		Total			Quadrupole
State[a]	length (Å)	*s* like	*p* like	*d* like	electronic	Nuclear	Total	splitting (mm/sec)
$^3\Sigma_g$	2.0	−0.2791	−0.0482	−5.0297	−5.357	0.963	−4.394	−3.65
$^3\Sigma_g$	1.87	−0.3672	0.0404	−5.2287	−5.555	1.178	−4.377	−3.63
$^7\Sigma_g$	2.0	−0.2652	−0.0044	−3.8379	−4.107	0.963	−3.144	−2.61
$^7\Sigma_g$	1.87	−0.4392	−0.3693	−3.5446	−4.353	1.178	−3.175	−2.64
$^9\Sigma_g$	1.87	−0.9708	−0.3200	−1.7408	−3.032	1.178	−1.853	−1.54
$^7\Pi_u$	1.87	−0.4392	−0.3693	−2.8902	−3.699	1.178	−2.52	−2.09
$^7\Delta_u$	1.87	−0.5146	−0.3744	−1.8797	−2.769	1.178	−1.591	−1.32

[a] The electronic configurations for the various states are $^3\Sigma_g(\sigma_g^2\pi_u^4\delta_g^4\sigma_g^2(\sigma_u^*)^2(\pi_g^*)^2)$, $^7\Sigma_g(\sigma_g^2\pi_u^4\sigma_g^2\delta_g^2(\delta_u^*)^2(\pi_g^*)^2(\sigma_u^*)^2)$, $^9\Sigma_g(\sigma_g^2\pi_u^4\delta_g^2\sigma_g^2(\delta_u^*)^2(\pi_g^*)^2(\sigma_u^*)^1(\sigma_u^*)^1)$, $^7\Pi_u(\sigma_g^2\pi_u^4\sigma_g^2\delta_g^2(\delta_u^*)^2(\pi_g^*)^3(\sigma_u^*)^1)$, and $^7\Delta_u(\sigma_g^2\pi_u^4\sigma_g^2\delta_g^3(\delta_u^*)^2(\pi_g^*)^2(\sigma_u^*)^1)$.

EFG. The outermost p orbitals in the free atom occur as a closed $3p$ shell with no anisotropy. In the molecule, however, they can admix either with $3d$ orbitals or with empty $4p$ orbitals to produce finite EFG's. Since the valence $4s$ and $3d$ states in the atom are closer in energy we expect stronger mixing between them than between the core $3p$ and the $3d$ states. The significant decrease in EFG in going to the higher-spin multiplet states appears to be caused primarily by a decrease in the $3d$ contribution, a consequence of the tendency towards more spherical symmetry due to greater equality of populations in the various d states of majority spin. The other notable feature of the results in Table I is the rather small variation in the net EFG in going from the bond distance of 1.87 to 2.0 Å. The total electronic contribution as well as the individual ones are seen to vary somewhat more significantly but they are counteracted by the change in the nuclear contribution.

The major conclusion that one arrives at from Table I is that the $^3\Sigma_g$ leads to quadrupole splitting closest to (about 90% of) the experimental value of -4.05 ± 0.04 mm/sec. The state that leads to the next closest quadrupole splitting as compared to experiment[19] is the $^7\Sigma_g$ state, about 65%. All the other states lead to substantially smaller quadrupole splittings. This result is of course based on a Hartree-Fock calculation without incorporation of many-body effects. However, first-principle many-body calculations[39] on quadrupole interactions in atomic systems have indicated that such effects are not of crucial importance for this property.

Thus, on the basis of the observed quadrupole splitting from Mössbauer measurements, the $^3\Sigma_g$ state of Fe_2 seems to be the favored one. This is in keeping with the general conclusions from analysis[11,12] of spectroscopic data and configuration interaction[13] calculations that ground states of transition metal diatomic systems favor low spin.

In the rest of the section we shall discuss the results of our Hartree-Fock investigations on the other two properties, isomer shift and hyperfine field, available from Mössbauer spectroscopy measurements.[19] It should be remarked that unlike the quadrupole interaction which involves only the anisotropy of the charge distribution around the nucleus, the other two properties involve combinations of a number of factors such as direct and exchange, contact and dipolar, contributions in the case of the hyperfine field[35,40] and the difference in the charge densities at the ^{57m}Fe nucleus in Fe_2 and a reference system in the case of the isomer shift.[30,31,41] One should therefore use these properties for further tests of conclusions derived from analysis of quadrupole interactions, rather than make judgements from them alone.

Considering the isomer shift first, the second and fourth columns of Table II list for the $^3\Sigma_g$ and $^7\Sigma_g$ states the differences in electron densities between individual s-like molecular orbitals in Fe_2 and the corresponding atomic shells in the neutral atom obtained using the same Gaussian basis set in both cases. For $1s$-, $2s$-, and $3s$-type molecular orbitals the bonding as well as antibonding states are occupied and their contributions are both included in the electron density. For the $4s$ orbital, only the bonding state is occupied. As can be seen from Table II, there is also some contribution from what we call the non-s orbitals. The major components of these orbitals are p and d like but they also have some s admixtures which lead to finite densities at the nucleus, an effect which is absent in the atom. Another contribution that is absent in the atomic system, but is present in the molecule, is the density at the nucleus arising from the tails of the orbitals on the other atom. The combined contribution from these effects is seen to be quite significant, about 20% of the total $\delta(\rho_\uparrow+\rho_\downarrow)$ in the case of the $^3\Sigma_g$ state.

It appears in general from Table II that the molecular orbital densities from individual shells are lower for the $^7\Sigma_g$ state as compared to $^3\Sigma_g$. As a result of this, the density for the molecule is larger than for the neutral atom in the $^3\Sigma_g$ state while it is smaller for the $^7\Sigma_g$. This effect could at least partly be a consequence of the greater exchange (attraction) interaction between core and unpaired spin orbitals with parallel spin in the high-spin state as compared to the low-spin state, leading[25,35] to a "drawing outwards" of the electron density due to the core states. This same effect leads to the larger unpaired spin density for the $^7\Sigma_g$ state as compared to $^3\Sigma_g$, which influences the hyperfine fields for the two systems, to be discussed later in this section.

In comparing the experimental isomer shift with theory, it is preferable to consider the isomer shift between Fe_2 and the ionic crystal K_3FeF_6. This is because the electron density in iron metal is difficult to calculate accurately. Thus, since the isomer shift of K_3FeF_6 with respect to iron metal has been measured[42] to be 0.42

TABLE II. Charge and spin densities at ^{57m}Fe from various orbitals in Fe_2, all expressed in atomic units (a_0^{-3}).

Molecular orbitals	$^3\Sigma_g$		$^7\Sigma_g$	
	$\delta(\rho_\uparrow+\rho_\downarrow)$[a]	$\rho_\uparrow-\rho_\downarrow$	$\delta(\rho_\uparrow+\rho_\downarrow)$[a]	$\rho_\uparrow-\rho_\downarrow$
1s±1s	1.1796	−0.0302	0.7423	−0.0512
2s±2s	3.0208	−0.7173	2.1432	−1.7457
3s±3s	0.7944	0.4476	−3.0742	0.8114
4s+4s	−2.5936	0.0122	−3.4171	0.3464
Non-s orbitals	0.3266	−0.0571	−0.4665	−0.0098
Total	2.7278	−0.3448	−4.0723	−0.6489

[a] Refers to the difference between the densities from the molecular orbitals in Fe_2 and the corresponding orbitals of Fe^0.

mm/sec, one can combine this with the observed isomer shift between Fe_2 and iron metal of -0.14 mm/sec to obtain

$$[\varepsilon(\mathrm{Fe_2})-\varepsilon(\mathrm{K_3FeF_6})]_{\mathrm{expt}}=-0.56\ \mathrm{mm/sec}\ . \tag{9}$$

Since the density differences given in Table II referred to those between Fe_2 and Fe^0 one needs the density difference $\rho(\mathrm{Fe^0})-\rho(\mathrm{K_3FeF_6})$ to derive $\rho(\mathrm{Fe_2})-\rho(\mathrm{K_3FeF_6})$. Fortunately the former can be obtained from earlier Hartree-Fock calculations.[43] Thus,

$$\rho(\mathrm{Fe^0})-\rho(\mathrm{Fe^{+2}})=3.107\ e\,a_0^{-3} \tag{10}$$

and

$$\rho(\mathrm{Fe^{+2}})-\rho(\mathrm{K_3FeF_6})=-4.118\ e\,a_0^{-3}\ , \tag{11}$$

leading to

$$\rho(\mathrm{Fe^0})-\rho(\mathrm{K_3FeF_6})=-1.011\ e\,a_0^{-3}\ . \tag{12}$$

Combining this with the values of $\rho(\mathrm{Fe_2})-\rho(\mathrm{Fe^0})$ for the $^3\Sigma_g$ and $^7\Sigma_g$ states in Table II and using Eq. (4), the theoretical values of the isomer shift for the two states come out as

$$[\varepsilon(\mathrm{Fe_2})-\varepsilon(\mathrm{K_3FeF_6})]_{\mathrm{theor}}=-0.515\ \mathrm{mm/sec}\ \ (^3\Sigma_g)\ , \tag{13}$$

$$[\varepsilon(\mathrm{Fe_2})-\varepsilon(\mathrm{K_3FeF_6})]_{\mathrm{theor}}=+1.525\ \mathrm{mm/sec}\ \ (^7\Sigma_g)\ . \tag{14}$$

The isomer shift for the $^3\Sigma_g$ state is seen to be in good agreement with the experimental result in Eq. (9), while the $^7\Sigma_g$ state yields an isomer shift of opposite sign as experiment[19] and substantially larger magnitude. This is a consequence of the smaller densities found for Fe_2 as compared to Fe^0 in Table II for the $^7\Sigma_g$ state. Thus the analysis of the isomer shift also supports the $^3\Sigma_g$ state as was found from the study of the quadrupole interaction.

Considering next the hyperfine field at the ^{57m}Fe nucleus, one needs to obtain the contact and dipolar contributions given, respectively, by Eqs. (7) and (8). Since the present work utilizes the UHF procedure, the wave functions corresponding to the majority and minority spin states are different for the doubly occupied orbitals, the difference in their contributions being referred to as the exchange polarization contribution[35,40] to the hyperfine field. For the singly occupied orbitals, of course, only the majority spin state is occupied and is the only one that contributes to the contact and dipolar fields, this contribution being referred to as the direct effect. The contact contributions, apart from the conversion factor in Eq. (7), are presented in the third and fifth columns of Table II for the $^3\Sigma_g$ and $^7\Sigma_g$ states. All the *s*-like orbitals are doubly occupied and so they contribute only to the exchange polarization effect. As in the case of the atom,[44] the 2*s* and 3*s* contributions are the dominant ones and have opposite sign. In the case of the $^3\Sigma_g$ state, the net hyperfine field is almost entirely determined by the 2*s*- and 3*s*-like contributions while for the $^7\Sigma_g$ state there is a significant contribution from the paired 4*s*-like orbital of the bonding type, the antibonding one being empty. The non-*s* contributions arise primarily from the 3*d*- and 3*p*-like orbitals (the 2*p*-like orbitals making negligible contributions). For the $^3\Sigma_g$ state, the only singly occupied orbitals are the $3d_{xz}$ and $3d_{yz}$ antibonding (π_g^*) orbitals and they have zero density at the nucleus leading to zero direct contact contribution. Thus the contact hyperfine field is contributed to entirely by the exchange polarization effect. The same conclusion also applies to the $^7\Sigma_g$ state because although the number of unpaired states is larger, they all make zero contributions to the contact hyperfine field.

The dipolar contributions from the various paired and unpaired orbitals are given in Tables III and IV for $^3\Sigma_g$ and $^7\Sigma_g$ states, respectively. Considering the $^3\Sigma_g$ first, the direct contribution arises from the unpaired π_g^* orbitals, which are composed primarily of $3d_{xz}$ and $3d_{yz}$ orbitals, and is seen to be positive. The contributions from the paired spin orbitals are seen to be different for states with opposite spin, their difference representing the exchange contribution to the dipolar field. The net exchange effect is seen to be positive, although significantly smaller than the direct effect, and adds to the latter, leading to a net positive dipolar field when the majority spin is aligned along the internuclear axis. Thus, for the $^3\Sigma_g$ state, the contact contribution (Table II) is seen to oppose the dipolar contribution.

For the $^7\Sigma_g$ state, where there are six unpaired spin states, the net direct contribution is seen from Table IV to consist of varying signs for the different states, the net contribution being negative. The net exchange contribution to the dipolar field on the other hand is seen to be positive leading to a reduction in magnitude of the net dipolar field as compared to the direct contribution. Also the contact and dipolar contributions are now seen to have the same sign and augment each other, in contrast to the case of the $^3\Sigma_g$ state.

Using the conversion factors in Eqs. (7) and (8) relating the contact and dipolar hyperfine fields to the spin density and the dipolar integrals, respectively, we obtain the following values for these fields. The dipolar field is listed for both the cases where the applied magnetic field is along the internuclear axis and perpendicular to it. For $^3\Sigma_g$ we have

$$\begin{aligned}
&H_{\mathrm{hf}}^{\mathrm{cont}}=-180.7\ \mathrm{kG}\,,\\
&(H_{\mathrm{hf}}^{\mathrm{dip}})_{\parallel}=119.5\ \mathrm{kG}\,,\\
&(H_{\mathrm{hf}}^{\mathrm{dip}})_{\perp}=-\tfrac{1}{2}(H_{\mathrm{hf}}^{\mathrm{dip}})_{\parallel}=-59.8\ \mathrm{kG}\,,\\
&H_{\mathrm{hf}}^{\parallel}=H_{\mathrm{hf}}^{\mathrm{cont}}+(H_{\mathrm{hf}}^{\mathrm{dip}})_{\parallel}=-61.2\ \mathrm{kG}\,,\\
&H_{\mathrm{hf}}^{\perp}=H_{\mathrm{hf}}^{\mathrm{cont}}+(H_{\mathrm{hf}}^{\mathrm{dip}})_{\perp}=-240.5\ \mathrm{kG}\,,
\end{aligned} \tag{15}$$

and for $^7\Sigma_g$,

$$\begin{aligned}
&H_{\mathrm{hf}}^{\mathrm{cont}}=-340.2\ \mathrm{kG}\,,\\
&(H_{\mathrm{hf}}^{\mathrm{dip}})_{\parallel}=-203.1\ \mathrm{kG}\,,\\
&(H_{\mathrm{hf}}^{\mathrm{dip}})_{\perp}=-\tfrac{1}{2}(H_{\mathrm{hf}}^{\mathrm{dip}})_{\parallel}=+101.5\ \mathrm{kG}\,,\\
&H_{\mathrm{hf}}^{\parallel}=H_{\mathrm{hf}}^{\mathrm{cont}}(H_{\mathrm{hf}}^{\mathrm{dip}})_{\parallel}=-543.2\ \mathrm{kG}\,,\\
&H_{\mathrm{hf}}^{\perp}=H_{\mathrm{hf}}^{\mathrm{cont}}+(H_{\mathrm{hf}}^{\mathrm{dip}})_{\perp}=-238.6\ \mathrm{kG}\ .
\end{aligned} \tag{16}$$

As expected from the relative signs of the contact and dipolar contributions in Tables II, III, and IV just discussed, the net hyperfine field for the $^3\Sigma_g$ state parallel to

TABLE III. Dipolar contributions to the hyperfine field for $^3\Sigma_g$ state (in units of a_0^{-3}).

	Orbitals	$\langle X \rangle_\uparrow$[a]	$\langle X \rangle_\downarrow$	$\langle X \rangle_\uparrow - \langle X \rangle_\downarrow$
$[(\pi_g^*)^2]$	$3d_{xz}+3d_{xz}$	0.7937		0.7937
	$3d_{yz}+3d_{yz}$	0.7937		0.7937
	Total direct[b]	1.5874		
(π_u^4)	$3d_{xz}-3d_{xz}$	0.7187	0.5488	0.1699
	$3d_{yz}-3d_{yz}$	0.7187	0.5488	0.1699
$[\sigma_g^2,(\sigma_u^*)^2,\delta_g^4]$	Rest $3d$	0.4371	0.4701	−0.033
	Total s	0.1389	0.1401	−0.0012
	Total $2p$	−0.0658	0.2875	−0.3533
	Total $3p$	0.0979	−0.2714	0.3693
	Total exchange[c]	2.0455	1.7239	0.3216
	Total	3.6329	1.7239	1.909

[a] X stands for $(3\cos^2\theta-1)/r^3$.

[b] Represents net contribution from unpaired spin electrons.

[c] Represents exchange polarization contribution from paired spin electrons through their exchange with unpaired spin electrons.

the internuclear axis is seen to be smaller in magnitude than in the perpendicular direction, while the reverse is true for the $^7\Sigma_g$ case. This feature also appears to provide support for the choice of the $^3\Sigma_g$ as the ground state, as we have already found from analysis of the quadrupole interaction and isomer shift, since there appears to be experimental evidence[45] that the hyperfine field is larger in magnitude when the external field is applied perpendicular to the internuclear axis, which is the direction of the maximum field gradient component.

The signs of the net hyperfine fields for both states, and for applied field both parallel and perpendicular to the internuclear axis, are all seen from Eqs. (15) and (16) to be negative, determined by the sign of the contact field which is negative. It would be helpful to have experimental measurements of the sign of the hyperfine field in the future to test this aspect of the theory. The magnitude of the hyperfine field for the $^3\Sigma_g$ state in the direction perpendicular to the internuclear axis appears from theory to be less than half the experimental value.[19] This feature is in contrast with the very good agreement that has been found for the quadrupole interaction and isomer shift earlier in this paper. From many-body calculations in atomic systems, correlation effects have been seen to be rather important for hyperfine fields[24,40] and relatively unimportant for quadrupole interaction[39] and isomer shift.[41]

TABLE IV. Dipolar contributions to the hyperfine field for $^7\Sigma_g$ state (in units of a_0^{-3}).

	Orbitals	$\langle X \rangle_\uparrow$[a]	$\langle X \rangle_\downarrow$	$\langle X \rangle_\uparrow - \langle X \rangle_\downarrow$
(δ_g^2)	$3d_{x^2-y^2}+3d_{x^2-y^2}$	−1.3380		−1.3380
	$3d_{xy}+3d_{xy}$	−1.3380		−1.3380
$[(\delta_u^*)^2]$	$3d_{x^2-y^2}-3d_{x^2-y^2}$	−1.3822		−1.3822
	$3d_{xy}-3d_{xy}$	−1.3822		−1.3822
$[(\pi_g^*)^2]$	$3d_{xz}+3d_{xz}$	0.7305		0.7305
	$3d_{yz}+3d_{yz}$	0.7305		0.7305
	Total direct[b]	−3.9794		−3.9794
(σ_g^2)	$3d_{z^2}+3d_{z^2}$	1.4088	1.3807	0.0281
$[(\sigma_u^*)^2]$	$3d_{z^2}-3d_{z^2}$	1.4088	1.4084	−0.0004
(π_u^4)	$3d_{xz}-3d_{xz}$	0.6442	0.4650	0.1792
	$3d_{yz}-d_{yz}$	0.6442	0.4650	0.1792
	Total s	0.1204	0.1448	−0.0244
	Total p	0.1887	−0.1844	0.3731
	Total exchange[c]	4.4151	3.6795	0.7356
	Total	0.4357	3.6795	−3.2438

[a] X stands for $(3\cos^2\theta-1)/r^3$.

[b] Represents net contribution from unpaired spin electrons.

[c] Represents exchange polarization contribution from paired spin electrons through their exchange with unpaired spin electrons.

Since Fe_2 is a covalently bonded system it is difficult to draw conclusions regarding the nature of these contributions by analogy with atomic systems. The investigation of many-body effects in the molecular system would be rather difficult, but we hope however that such investigations will be carried out in the future to resolve the remaining difference between theory and experiment. It will also be useful in the future to analyze the difficult problems of the roles of relativistic effects and the influence of the neighboring argon atoms on hyperfine properties.

IV. CONCLUSION

The results of our first-principle self-consistent Hartree-Fock investigation of the ^{57m}Fe quadrupole interaction and isomer shift in Fe_2 molecule have provided strong support for $^3\Sigma_g$ as the ground state of this molecule. This conclusion is in agreement with the general conclusions from analysis[12] of optical and related data for transition-metal diatomics and accurate generalized valence bond calculations[13] of the energy for Cr_2 and Mo_2 molecules with many-body effects included through configuration interaction (CI).

In contrast to the quadrupole interaction and isomer shift which are relatively insensitive[39,41] to many-body effects, the latter are expected to be rather important in influencing the relatively small differences in energy between different multiplet states. The inclusion of many-body effects through configuration interaction[13] would entail substantial additional computational effort than that involved in the present work. We hope however that the results of our current investigation supporting the $^3\Sigma_g$ configuration for Fe_2 will stimulate efforts in the future to study total energies of the two multiplet states $^3\Sigma_g$ and $^7\Sigma_g$ (which provide results for e^2qQ and $\delta\varepsilon$ closer to experiment than other states) including many-body effects and make an independent decision about the ground state from energy considerations.[46]

Our detailed investigation of the contact and dipolar contributions to the hyperfine field tensor, including exchange polarization effects, also indicates support for the $^3\Sigma_g$ configuration by showing that the direction for the maximum component is perpendicular to the internuclear axis in agreement with evidence[45] in this respect from Mössbauer measurements. The calculated magnitudes of the hyperfine field components are however significantly smaller than experiment.[19] As has also been concluded from atomic many-body investigations,[40] the hyperfine field tensor is expected to be influenced markedly by many-body effects. It will be interesting in the future to study these effects through UHF-CI investigations which will also allow a determination of the total energy, whose importance has been discussed in the preceding paragraph.

Lastly, it should be emphasized that this investigation, in common with earlier investigations[11,13–16] on the properties of transition-metal diatomics, deals with the isolated molecule. The experimental data[19] associated with the nuclear properties studied here are however measured for trapped molecules in rare-gas solids. It will be of interest in the future to carry out the time consuming, but useful, Hartree-Fock cluster investigations including neighboring rare-gas atoms to study the influence of the environment on hyperfine properties.

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[46] That the inclusion of many-body effects is important for the total energy, especially for the difference between two multiplet states can be seen from the total energies we have obtained for the $^3\Sigma_g$ and $^7\Sigma_g$ states, namely -2524.22 a.u. and -2524.35 a.u., respectively. The total energy of the $^7\Sigma_g$ is actually lower in the Hartree-Fock approximation than $^3\Sigma_g$ as one would expect from the stronger exchange in the former case. It would be very interesting to see if many-body calculations in the future will provide correlation effects that reverse the order of the total energies to make the $^3\Sigma_g$ lower in energy and therefore the ground state as the interpretation of the hyperfine and isomer shift data in the present work indicates.