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# Relativistic electron densities and isomer shifts of $^{57}$Fe in iron-oxygen and iron-fluorine clusters and of iron in solid noble gases*

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Relativistic calculations of various electronic configurations of the iron atom are used in conjunction with Huckel-type molecular-orbital and limited-configuration-interaction calculations of iron-containing clusters to determine electron densities at the iron nucleus. The calculations include all effects of the overlap of iron core and ligand orbitals, and the effect of potential distortion of iron-core orbitals due to molecular configurations $3d^m\,4s^n$. Using the calculated electron densities and experimental isomer shifts, the relative change in the $^{57}$Fe nuclear-charge radius is deduced from studies of $\mathrm{FeO_6}^{-9}$ and $\mathrm{FeO_6}^{-10}$ as $(-8.72 \pm 1.02) \times 10^{-4}$, from studies of $\mathrm{FeF_6}^{-3}$ and $\mathrm{FeF_6}^{-4}$ as $(-9.18 \pm 0.56) \times 10^{-4}$, and from iron monomers and dimers dissolved in solid noble gases as $(-7.12 \pm 0.59) \times 10^{-4}$ or $(-8.65 \pm 0.71) \times 10^{-4}$, depending upon the assumed dimer geometry. From all these studies we obtain for the relative change in charge-radius value an average of $(-8.85 \pm 0.9) \times 10^{-4}$, in reasonable agreement with the work of several other investigators.

## I. INTRODUCTION

Many theoretical estimates have been made of the electron densities at iron nuclei, $\rho(0)$, in various compounds with the aim of relating the densities with the corresponding isomer shifts $\delta$ obtained from experimental Mössbauer investigations of compounds containing the isotope $^{57}$Fe. A key aim has been to obtain an accurate calibration of the relationship between the observed isomer shifts and electron-density differences in solids in order to obtain valuable information for application in various systems. However, these electron-density calculations have included relativistic effects only to the extent that they could be described by a simple correction factor, and the final correlations between $\rho(0)$ and $\delta$ have not been as unambiguous as might be desirable. In this communication we investigate the role of relativistic effects by means of Dirac-Fock calculations and show that a more careful inclusion of relativistic effects, iron inner-shell contributions, and direct ligand contributions can lead to a more satisfactory correlation of electronic densities and isomer shifts in iron compounds.

The quantities $\rho(0)$ and $\delta$ are related to each other by the formula[1]

$$\delta = C(\delta R/R)[\rho_{\mathrm{abs}}(0) - \rho_{\mathrm{source}}(0)] \quad , \qquad (1)$$

where $\rho_{\mathrm{abs}}(0)$ and $\rho_{\mathrm{source}}(0)$ are the electron densities at the absorber and the source, respectively, and the constant $C$ has the value $0.282\times10^3 a_0^3$ mm sec$^{-1}$. In previous work the charge densities were obtained by nonrelativistic calculations, and were then adjusted to include relativistic effects through multiplication by a factor $S'(Z)$ which for iron was taken as 1.3.[1] The alternative which we shall pursue here is to use values of $\rho(0)$ obtained from calculations in which relativistic effects were included directly.

## II. MOLECULAR-ORBITAL CALCULATIONS

The calculations to be reported here are for iron-oxygen and iron-fluorine compounds, and for Fe-Fe dimers in solid noble gases. These systems have "high-spin" ground states necessarily having singly occupied molecular orbitals (MO's), and we found it advisable to proceed in a way which might keep the calculations from becoming unduly complicated. Our procedure essentially consisted of a sequence of three steps.

(i) First, we carried out an extended-Hückel self-consistent-field calculation for a hypothetical state consisting only of the lowest-energy doubly occupied orbitals, for the purpose of defining a suitable orthonormal set of valence MO's. The atomic-orbital basis was restricted to valence atomic orbitals, and specifically to Fe $3d$, $4s$, and $4p$ orbitals and to ligand $2s$ and $2p$ orbitals. The other Fe orbitals ($1s$, $2s$, $2p$, $3s$, $3p$) were not included at this stage of the calculations, and it was assumed that they were fully occupied and affected the valence calculations only through the Fe Hückel parameters. Corresponding assumptions were made for the omitted ligand $1s^2$ cores. The exact procedure used for the extended-Hückel calculations and the parameter values used for iron, fluorine, and oxygen are given elsewhere.[2]

(ii) Our second step was to carry out a spin-projected configuration-interaction (CI) study for the valence electrons considered in step (i), using the Hückel MO's as basis, and requiring the overall wave function to be a spin eigenfunction of suitable quantum numbers. For the cubic ferrous high-spin compounds, the CI included configurations of occupancy types $d_t^4 d_e^2$ and $d_t^3 d_e^3$, where $d_t$ and $d_e$ refer to MO's which are predominantly of Fe $3d$ character and, respectively, of $t$ and $e$ symmetry. For the cubic ferric compounds, configurations of occupancy type $d_t^3 d_e^2$ were used. In each case the configurations consisted of those linear combinations of Slater determinants needed to describe properly the spin eigenstate. Matrix elements between spin-projected configurations were calculated as described elsewhere,[3] with all necessary integrals evaluated by customary approximations which take into consideration the atomic cores. Details of this procedure have been reported elsewhere.[2]

From our calculations we obtained the first-order density matrix of the CI valence-electron wave function, and thus the contribution to $\rho(0)$ from the valence-electron distribution. Letting $P_{ab}$ be the density-matrix element connecting normalized basis orbitals $\psi_a$ and $\psi_b$, the valence contribution to $\rho(0)$ takes the form

$$\rho_{\text{valence}}(0)=\sum_{a,b} P_{ab}\psi_a^*(0)\psi_b(0) \ , \tag{2}$$

where the sum is over the entire valence basis set. Another resultant of this second step is the determination of the occupancy of the Fe $3d$ and $4s$ orbital in the CI wave function. These occupancies are needed to estimate the potential distortion of iron orbitals due to the shielding experienced by the electrons on the Fe atom, and thereby to obtain reliable values of $\rho(0)$ for the Fe orbitals $1s$, $2s$, $3s$, and $4s$.

(iii) The third and final step in the calculation of $\rho(0)$ was to include in the electron density the effect of the omitted Fe orbitals. [The ligand $1s$ orbitals could also have been included but were not, as their effect on $\rho(0)$ would be negligible.] Because the Fe core orbitals are not orthogonal to all the occupied MO's of the CI, the electron density suffers a more complicated change than the addition of a contribution reflecting full occupancy of the core orbitals. In the procedure we follow here, the core orbitals are orthogonalized to the occupied valency MO's (and kept normalized and orthogonal to each other) before the charge density is calculated. There is a minor approximation involved in this orthogonalization when the valence wave function involves singly occupied orbitals. We actually orthogonalized all core orbitals to all valence orbitals occupied by any electron in any configuration.

If $\phi_1, \ldots, \phi_n$ are the occupied orthonormal valence orbitals to which the Fe core orbitals are to be orthogonalized, and if the orthogonalization is carried out in the order $3s$, $2s$, $1s$, we have

$$\begin{aligned}
\phi_{3s}&=N_{3s}\left(\psi_{3s}-\sum_{i=1}^{n}\langle\phi_i|\psi_{3s}\rangle\phi_i\right) \ , \\
\phi_{2s}&=N_{2s}\left(\psi_{2s}-\sum_{i=1}^{n}\langle\phi_i|\psi_{2s}\rangle\phi_i-\langle\phi_{3s}|\psi_{2s}\rangle\phi_{3s}\right) \ , \\
\phi_{1s}&=N_{1s}\left(\psi_{1s}-\sum_{i=1}^{n}\langle\phi_i|\psi_{1s}\rangle\phi_i-\langle\phi_{3s}|\psi_{1s}\rangle\phi_{3s}\right. \\
&\qquad\left.-\langle\phi_{2s}|\psi_{1s}\rangle\phi_{2s}\right) \ ,
\end{aligned} \tag{3}$$

where $\psi_{3s}$, $\psi_{2s}$, $\psi_{1s}$ are the original Fe core orbitals and $N_{3s}$, $N_{2s}$, and $N_{1s}$ are normalization factors. [We could continue, obtaining $\phi_{3p}$ and $\phi_{2p}$, but their contributions to $\rho(0)$ would be negligible.] The normalization conditions yield

$$\begin{aligned}
N_{3s}&=\left(1+\sum_{i=1}^{n}|\langle\phi_i|\psi_{3s}\rangle|^2\right)^{-1/2} \ , \\
N_{2s}&=\left(1+\sum_{i=1}^{n}|\langle\phi_i|\psi_{2s}\rangle|^2+|\langle\phi_{3s}|\psi_{2s}\rangle|^2\right)^{-1/2} \ , \\
N_{1s}&=\left(1+\sum_{i=1}^{n}|\langle\phi_i|\psi_{1s}\rangle|^2+|\langle\phi_{3s}|\psi_{1s}\rangle|^2\right. \\
&\qquad\left.+|\langle\phi_{2s}|\psi_{1s}\rangle|^2\right)^{-1/2} \ .
\end{aligned} \tag{4}$$

The core contribution to $\rho(0)$ is then

$$\rho_{\text{core}}(0)=2|\phi_{3s}(0)|^2+2|\phi_{2s}(0)|^2+2|\phi_{1s}(0)|^2 \ . \tag{5}$$

We complete the specification of the calculations by indicating how the values of $\psi(0)$ and of the overlap integrals occurring in Eqs. (3) and (4) were obtained.

Fully relativistic mixed-configuration Dirac-Fock calculations[3] were carried out for various Fe $3d^m 4s^n$ configurations, leading to the $|\psi(0)|^2$ values shown in Table I. [In these calculations, the relativistic analog of Hartree-Fock equations, i.e., the Dirac-Fock equations, are solved self-consistently for the four-component spinors, each expressible in terms of two radial functions $P(r)$ and $Q(r)$ which are, respectively, their major and minor components. Exchange is treated exactly

TABLE I. Electron densities (in $a_0^{-3}$) for iron as derived from fully relativistic mixed-configuration Dirac-Fock calculations, and for comparison as derived from nonrelativistic calculations by setting $c$ equal to infinity.

| Configuration | $3d^7 4s^1$ | $3d^7$ | $3d^6 4s^1$ | $3d^6$ | $3d^5 4s^1$ | $3d^5$ |
|---|---|---|---|---|---|---|
| Relativistic | | | | | | |
| $\lvert\psi_{1s}(0)\rvert^2$ | 6799.0179 | 6799.0543 | 6798.8811 | 6798.9179 | 6798.6529 | 6798.6876 |
| $\lvert\psi_{2s}(0)\rvert^2$ | 644.2989 | 644.2595 | 644.2315 | 644.1698 | 644.2254 | 644.1526 |
| $\lvert\psi_{2P_{1/2}}(0)\rvert^2$ | 3.4619 | 3.4622 | 3.4609 | 3.4613 | 3.4601 | 3.4608 |
| $\lvert\psi_{3s}(0)\rvert^2$ | 87.7530 | 87.4773 | 88.7276 | 88.4802 | 90.3804 | 90.2056 |
| $\lvert\psi_{3P_{1/2}}(0)\rvert^2$ | 0.4490 | 0.4481 | 0.4564 | 0.4565 | 0.4686 | 0.4697 |
| $\lvert\psi_{4s}(0)\rvert^2$ | 3.0918 | | 5.5751 | | 8.2129 | |
| Nonrelativistic | | | | | | |
| $\lvert\psi_{1s}(0)\rvert^2$ | | | | 5387.766 | | 5387.596 |
| $\lvert\psi_{2s}(0)\rvert^2$ | | | | 495.453 | | 495.429 |
| $\lvert\psi_{3s}(0)\rvert^2$ | | | | 67.662 | | 68.966 |

and mixed-configuration solutions are found (rather than the usual single-configuration solution) in order to minimize the error associated with $j$-$j$ coupling schemes.] Table I also contains for later comparison the results of some corresponding nonrelativistic calculations. Values of $\psi(0)$ for the actual orbital occupancies found in our CI calculations were determined by linear interpolation in $|\psi(0)|^2$ between the tabulated relativistic values. This interpolation procedure was checked by a separate direct and complete Dirac-Fock calculation with assumed occupation $3d^{5.6}$ and was found to be entirely satisfactory. The values of $\psi(0)$ for the ligand orbitals were obtained using Slater-type orbitals; as will be seen later these $\psi(0)$ values are nearly negligible and the uncertainties associated with the orbital choice are not important. The Fe-ligand overlap integrals[4] were calculated using Hartree-Fock Fe orbitals appropriate to the orbital occupancy,[5] and Hartree-Fock orbitals were used for[5] $F^-$ and for[6] $O^{--}$.

In evaluating $\rho(0)$, considerable practical simplification results from the small size of the overlap integrals between Fe core and ligand orbitals, and from the smallness of the ligand orbital amplitudes at the Fe nucleus. For example, typical maximum values of Fe-ligand overlap integrals are $\langle \text{Fe } 3s\,|\text{ligand}\rangle = 0.08$, $\langle \text{Fe } 2s\,|\text{ligand}\rangle = 0.02$, $\langle \text{Fe } 1s\,|\text{ligand}\rangle = 0.002$, while a typical value of $\psi_{\text{ligand}}(0)$ is 0.003 a.u. We shall be interested in obtaining $\rho(0)$ to within about 0.01 a.u., so that the foregoing figures enable us to eliminate from Eq. (2) all terms except the single contribution $P_{4s,4s}\,|\psi_{4s}(0)|^2$.

The foregoing figures together with the approximate magnitudes of $\psi_{1s}(0)$, $\psi_{2s}(0)$, and $\psi_{3s}(0)$ (cf. Table I) also indicate that in the evaluation of Eqs. (3) the substitution of $\phi_{3s}$ into the formula for $\phi_{2s}$, and that of $\phi_{3s}$ and $\phi_{2s}$ into the formula for $\phi_{1s}$, may be carried out neglecting terms which are cubic in the Fe-ligand overlaps. In evaluating Eqs. (4), the same approximations may apply. We then have the working formulas

$$\phi_{3s} = N_{3s}\left(\psi_{3s} - \sum_{i=1}^{n} \langle \phi_i | \psi_{3s}\rangle \phi_i\right) ,$$

$$\phi_{2s} = N_{2s}\left(\psi_{2s} - \sum_{i=1}^{n} \langle \phi_i | \psi_{2s}\rangle \phi_i + N_{3s}^2 \sum_{i=1}^{n} \langle \psi_{3s} | \phi_i\rangle \times \langle \phi_i | \psi_{2s}\rangle \psi_{3s}\right) , \tag{6}$$

$$\phi_{1s} = N_{1s}\left(\psi_{1s} - \sum_{i=1}^{n} \langle \phi_i | \psi_{1s}\rangle \phi_i + N_{3s}^2 \sum_{i=1}^{n} \langle \psi_{3s} | \phi_i\rangle \times \langle \phi_i | \psi_{1s}\rangle \psi_{3s} + N_{2s}^2 \sum_{i=1}^{n} \langle \psi_{2s} | \phi_i\rangle \langle \phi_i | \psi_{1s}\rangle \psi_{2s}\right) ;$$

$$N_{3s} = \left(1 + \sum_{i=1}^{n} |\langle \phi_i | \psi_{3s}\rangle|^2\right)^{-1/2} ,$$

$$N_{2s} = \left(1 + \sum_{i=1}^{n} |\langle \phi_i | \psi_{2s}\rangle|^2\right)^{-1/2} , \tag{7}$$

$$N_{1s} = \left(1 + \sum_{i=1}^{n} |\langle \phi_i | \psi_{1s}\rangle|^2\right)^{-1/2} .$$

Use of these formulas will cause $\rho(0)$ to contain all the cross-term contributions of the type $\psi_{ns}(0) \times \psi_{ms}(0)$ which have previously been identified as significant,[7-9] plus many additional terms of marginal importance. Equations (6) and (7) are finally reduced to expressions involving MO coefficients and basic atomic orbitals by substituting the linear

TABLE II. Experimental isomer shifts $\delta$, calculated electronic configurations for iron, and calculated electron densities $\rho_{ns}(0)$ at the Fe nucleus for various iron-containing compounds.

| Compound | $FeO_6^{-9}$ | $FeO_6^{-10}$ | $FeF_6^{-3}$ | $FeF_6^{-4}$ | Fe monomer | Fe dimer | |
|---|---|---|---|---|---|---|---|
| Expt. $\delta$ (mm/sec) | $0.50\pm0.05$[a] | $1.10\pm0.02$[a] | $0.77\pm0.02$[b] | $1.42\pm0.02$[b] | $-0.75\pm0.03$[c] | $-0.14\pm0.02$[c] | |
| Configuration | $3d^{5.70}4s^{0.169}$ | $3d^{6.27}4s^{0.157}$ | $3d^{6.41}4s^{0.13}$ | $3d^{6.62}4s^{0.14}$ | $3d^64s^2$ [d] | $3d^{5.88}4s^{1.38}$ [e] | $3d^{5.88}4s^{1.45}$ [f] |
| $\rho_{1s}(0)$ $(a_0^{-3})$[g] | 13602.64 | 13601.63 | 13601.84 | 13600.07 | 13597.66 | 13597.68 | 13597.68 |
| $\rho_{2s}(0)$ $(a_0^{-3})$ | 1275.98 | 1279.09 | 1280.21 | 1283.24 | 1288.55 | 1288.5 | 1288.52 |
| $\rho_{3s}(0)$ $(a_0^{-3})$ | 187.85 | 183.62 | 184.18 | 180.44 | 177.95 | 178.0 | 178.07 |
| $\rho_{4s}(0)$ $(a_0^{-3})$ | 1.08 | 0.77 | 0.59 | 0.56 | 11.15 | 8.1 | 8.54 |

[a] Reference 15. Values of $\delta$ at 300 K (versus sodium ferrocyanide at 300 K) are derived from a $^{60}Co$-$\gamma$-irradiated $^{57}Fe$-doped MgO sample; Debye temperatures for $FeO_6^{-9}$ and $FeO_6^{-10}$ are both ~400 K.

[b] Reference 11. Values of $\delta$ at 300 K (versus sodium ferrocyanide at 300 K) are derived from a $^{60}Co$-$\gamma$-irradiated $^{57}Fe$-doped $KMgF_3$ sample; Debye temperatures for $FeF_6^{-3}$ and $FeF_6^{-4}$ are both ~400 K.

[c] Reference 16. Values of $\delta$ at 1.45 K (versus $\alpha$-iron at 300 K).

[d] Configuration $3d^64s^2$ for an iron monomer in solid noble gases is assumed.

[e] Configuration $3d^{5.88}4s^{1.38}$ corresponds to a Fe-Fe distance of 3.99 Å, equal to the nearest-neighbor distance in pure solid Kr at 4.2 K (see Ref. 10).

[f] Configuration $3d^{5.88}4s^{1.45}$ corresponds to a Fe-Fe distance of 4.20 Å (see Ref. 10).

[g] Values of $\rho_{ns}(0)$ as derived from Eqs. (2), (6), and (7) of the text, corresponding to overlap integrals calculated with Hartree-Fock atomic orbitals of Fe $3d^6$ (Ref. 5) and $F^-$ (Ref. 5) for $FeF_6^{-3}$; Fe $3d^7$ (Ref. 5) and $F^-$ (Ref. 5) for $FeF_6^{-4}$; Fe $3d^5$ (Ref. 5) and $O^{--}$ (Ref. 6) for $FeO_6^{-9}$; Fe $3d^6$ (Ref. 5) and $O^{--}$ (Ref. 6) for $FeO_6^{-10}$; and iron-ligand interatomic distances $FeF_6^{-3}$: 1.85 Å (Ref. 9); $FeF_6^{-4}$: 2.06 Å (Ref. 17); $FeO_6^{-9}$: 2.00 Å (Ref. 7); and $FeO_6^{-10}$: 2.12 Å (Ref. 18).

combinations found in step (i) of the calculations:

$$\phi_i = \sum_a C_{ai}\psi_i \quad . \tag{8}$$

## III. RESULTS AND DISCUSSION

The calculational methods described here were applied to the six systems listed in Table II; this table also lists the individual and total values of $\rho(0)$. In addition, we give the experimental values of $\delta$ and the electronic configurations found for Fe in our calculations. The main use we shall make of these results is in the determination of the factor $\delta R/R$ appearing in Eq. (1). The procedure least likely to be affected by systematic uncertainties in $\rho(0)$ is that of obtaining $\delta R/R$ by relating differences $\Delta\delta$ and $\Delta\rho$ between similar systems, according to the equation

$$\Delta\delta = C(\delta R/R)\,\Delta\rho(0) \quad . \tag{9}$$

Before using the data in Table II, let us make some preliminary observations. First, we note from the tabular entries that changes in $\rho(0)$ associated with the Fe 1s and 2s orbitals could not have been neglected. Next, turning to the electron densities reported in Table I, we see by comparing relativistic and nonrelativistic densities that they are related by a correction factor $S'(Z) \equiv |\psi_{\rm rel}(0)|^2/|\psi_{\rm nonrel}(0)|^2$, which is approximately 1.262 for Fe 1s electrons, 1.300 for Fe 2s electrons, and 1.308 for Fe 3s electrons. These numbers are relatively insensitive to orbital occupancy, and indicate that it would not have led to serious error to have used corrected $[S'(Z)=1.3]$ nonrelativistic calculations of $|\psi(0)|^2$.

We have previously studied iron monomer and dimer in solid noble gases,[10] and iron-fluorine clusters[2,11]; the present results indicate that our previously obtained $\delta R/R$ values should be recalculated including the Fe 1s and 2s and ligand orbital contributions. In the case of the iron-fluorine clusters, recent information provided by Duff[9] also suggests that our previously used Fe-F distance of 1.94 Å in $FeF_6^{-3}$ may be too large, and that a better value for this distance is 1.85 Å. Using this change in geometry we find a reduced value for $\delta R/R$.

Proceeding to the $\delta R/R$ determinations, we find from $FeO_6^{-9}$ and $FeO_6^{-10}$ the value $(-8.72\pm1.02)\times10^{-4}$. From the clusters $FeF_6^{-3}$ and $FeF_6^{-4}$, using Duff's geometry, we find for $\delta R/R$ the value $(-9.18\pm0.56)\times10^{-4}$, in significant contrast to our earlier value[11] of $-12.46\times10^{-4}$. Finally, comparing Fe monomer and dimer in solid noble gases, we have two sets of results which differ in the assumptions made as to the Fe-Fe distance in the dimer. If we take the Fe-Fe distance as the nearest-neighbor separation of 3.99 Å in pure solid Kr at 4.2 K, we obtain $\delta R/R = (-7.12\pm0.59)\times10^{-4}$. However, if we use the alternately suggested Fe-Fe distance[18] of 4.20 Å, we obtain $\delta R/R = (-8.65\pm0.71)\times10^{-4}$. The results for iron in solid noble gases are also subject to the approximation that we did not take into account interactions involving neighboring noble-gas atoms; this is a cruder approximation than that used by Walch and Ellis[12] in their recent work. The $\delta R/R$ values from iron-dimer and iron-monomer studies are therefore somewhat less reliable than those obtained from the other system.

Since the values of $\delta R/R$ estimated from the Fe-O clusters, the Fe-F clusters, and from iron in solid noble gases should agree, we were gratified to note that the ranges of $\delta R/R$ from the different calculations do indeed overlap. In fact, combining our different sets of results, we conclude that our most probable value of $\delta R/R$ is $-8.85\times10^{-4}$, with a probable error of about $\pm 0.9 \times 10^{-4}$. This value is in very good agreement with those obtained in the most recent calculations, namely, the value $(-8.87\pm1.07)\times10^{-4}$ deduced by Regnard and Pelzl.[13] It is somewhat larger in magnitude than the values which had been reported previously by other investigators.[14]

The present study contains several significant refinements, not all of which have previously been included simultaneously. First, the results of molecular-orbital calculations are used to define valence contributions to $\rho(0)$, according to Eq. (2). Second, overlap distortion of the $s$ orbitals in the iron core by ligand valence orbitals has been handled as described in Eqs. (6) and (7). In addition, potential distortion of the iron core $s$ orbitals has been taken into account insofar as the distortion is produced by changes in the electron distribution at the iron atom. This distortion is treated by using Dirac-Fock atomic orbitals appropriate to the electronic configurations $3d^m4s^n$ found in the configuration-interaction calculations. However, the calculations do not include polarization of the iron core orbitals by direct electrostatic interaction with charge on neighboring ligands. This effect should be considerably smaller than those which were included. Another small effect which was not included in the study is the contribution to $\rho(0)$ from relativistic effects upon the $2p$ and $3p$ orbitals (cf. Table I). While the contributions to $\rho(0)$ are individually significant, their differences are so small that they would only have affected $\Delta\rho(0)$ in the third decimal place. We believe that the calculations presented here contain the main effects likely to influence the values found for $\Delta\rho(0)$, and that the quality of the results is probably now limited by the approximations inherent in simple molecular-orbital methods. As such methods have been found quite satisfactory for discussing charge distributions and their changes among analogous compounds, there is reason to expect the present results to be qualitatively correct.

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