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Properties and applications of the *average* interparticle distance

J. W. Hollett · R. A. Poirier

Abstract The first and second moment operators are used to define the origin invariant shape and size of a molecule or functional group, as well as expressions for the distance between two electrons and the distance between an electron and a nucleus. The measure of molecular size correlates quite well with an existing theoretical measure of molecular volume calculated from isodensity contours. Also, the measure of size is effective in predicting steric effects of substituents which have been measured experimentally. The electron-electron and electron-nuclear distances are related to components of the Hartree-Fock energy. The *average* distance between two-electrons can model the Coulomb energy quite well, especially in the case of localized molecular orbitals. The *average* distance between an electron and a nucleus is closely related to the electron-nuclear attraction energy of a molecule.

Keywords Coulomb integral · Localized molecular orbital · Molecular volume · Second moment · Steric effects

Introduction

It is generally useful to have simple physical interpretations of the theoretical electronic structure of a molecule. Specifically, the classification of molecular orbitals(MOs) as bonds, cores, and lone pairs, provides a picture of the electronic structure which is easily understood. Such a picture is obtained through localization of molecular orbitals [1, 2]. The molecular orbitals obtained through

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solving the Hartree-Fock equations are known as canonical molecular orbitals(CMOs) and while they collectively exhibit the symmetry of the molecule (belong to irreducible representations), they are delocalized over several atoms. However, molecular orbitals may be localized by a unitary transformation, using methods such as Boys [1] or Ruedenberg-Edmiston [2] localization. The localized molecular orbitals(LMOs) may then be used to investigate properties of a molecule which are not as conspicuous in CMOs.

Following the introduction and development of molecular orbital localization methods, interesting properties of these orbitals were investigated and used to describe chemical phenomena. In 1973, Robb, Haines and Csizmadia used LMOs to define the "*size*" of an electron pair [3], $\langle r^2 \rangle_{Ra}$.

$$\langle r^2 \rangle_{R_a} = \left| \langle \psi_a | r^2 | \psi_a \rangle_0 - R_a^2 \right| \tag{1}$$

where r^2 is the second moment operator, ψ_a is a doubly occupied LMO, and R_a is the centroid of charge of the LMO,

$$|R_a| = \sqrt{\langle \psi_a | x | \psi_a \rangle_0^2 + \langle \psi_a | y | \psi_a \rangle_0^2 + \langle \psi_a | z | \psi_a \rangle_0^2}, \tag{2}$$

calculated at some point $R_0 = (x_0, y_0, z_0)$. Csizmadia also provided a definition of the shape of an LMO [4]. The second moment tensor of an LMO, Ω, with respect to its own centroid of charge, is defined as

$$\Omega = \begin{pmatrix} \left[\langle x^2 \rangle_0 - \langle x \rangle_0^2\right] \left[\langle xy \rangle_0 - \langle x \rangle_0 \langle y \rangle_0\right] \left[\langle xz \rangle_0 - \langle x \rangle_0 \langle z \rangle_0\right] \\ \left[\langle y^2 \rangle_0 - \langle y \rangle_0^2\right] \left[\langle yz \rangle_0 - \langle y \rangle_0 \langle z \rangle_0\right] \\ \left[\langle z^2 \rangle_0 - \langle z \rangle_0^2\right] \end{pmatrix}. \tag{3}$$

Diagonalizing the tensor,

$$U^+ \Omega U = \begin{pmatrix} \langle x'^2 \rangle & 0 & 0 \\ & \langle y'^2 \rangle & 0 \\ & & \langle z'^2 \rangle \end{pmatrix}, \tag{4}$$

results in three eigenvalues, $\langle x'^2 \rangle$, $\langle y'^2 \rangle$, and $\langle z'^2 \rangle$ which can be associated with the axes of an ellipsoid that describes the shape of the LMO. Although the shape of an LMO may have chemical implications, it is the size of an LMO which has been related to various other properties of molecules.

It has been found that the size of a localized molecular orbital can be related to different molecular energy components. In 1975, the size of an atomic orbital, $\langle r^2 \rangle_i$, was related to the orbital energy, ϵ_i, by an equation of the form

$$\left(\frac{1}{\varepsilon_i} \right) = m \langle r^2 \rangle_i + b \tag{5}$$

where m and b are fitting parameters [5]. The same equation was later extended to molecules, relating LMO energies to their size [6]. Correlation energy was also found to be related to the size of an atom or molecule. A relationship between correlation energy, E_{corr}, and the total size of an atom, $\langle r^2 \rangle$, is given by

$$\left(|E_{corr}| \langle r^2 \rangle \right)^\gamma = k(Z - \sigma), \tag{6}$$

where Z is the nuclear charge and γ, k, and σ are constants optimized for each isoelectronic series of ions [7]. In contrast, the total correlation energy of a molecule is related to LMO size, $\langle r^2 \rangle_i$, by the equation(in a.u.)

$$E_{corr} = -0.06593 \sum_{i=1}^{M} \langle r^2 \rangle_i^{-0.1958}, \tag{7}$$

where M is the total number of MOs [8]. The relationships between LMO size and orbital energy and correlation energy may not appear obvious, however a relationship between LMO size and steric effects should be expected.

When Robb et al. defined the size of an electron pair [3], they also investigated the energetics of rotation about the CO bond in FCH_2OH as related to the size of the LMOs. Later, the size of an LMO was used to investigate stereochemistry in Diels-Alder reactions. Poirier et al. were able to predict facial selectivity in Diels-Alder reactions of 5-substituted 1,3-cyclopentadienes using a steric factor, S_{CX}/R_{CX} [9], where X is the substituent, S_{CX} is the size of the C5-X bond, and R_{CX} is the distance between the centroid of the bond to C5.

The size of an LMO, which is calculated using first and second moment operators, can model properties which require much more extensive calculation, such as orbital energy and correlation energy. Also, this easily calculated property enables the theoretical prediction of complex stereochemistry which would be much more difficult by any other method, if not impossible. Such an idea can be extended to molecules and functional groups. Using a definition similar to the size and shape of an LMO, the size and shape of a molecule or functional group can be defined, which also provides a means of calculating molecular volume [10]. On the other hand, the definiton of the size of an LMO can also be generalized to include MO pairs, which may be regarded as an interelectronic distance [12]. Furthermore, the interelectronic distance may be modified to represent electron-nuclear distance. In either case, the first and second moment operators prove quite useful for modeling molecular properties.

Theoretical definition of the shape and size of a molecule or functional group

Similar to the second moment tensor of an LMO (Eq. 3), the second moment tensor of a molecule, S, calculated at some point $r_0 = (x_0, y_0, z_0)$, is given as

$$S = \begin{pmatrix} \langle x^2 \rangle_{r_0} & \langle xy \rangle_{r_0} & \langle xz \rangle_{r_0} \\ & \langle y^2 \rangle_{r_0} & \langle yz \rangle_{r_0} \\ & & \langle z^2 \rangle_{r_0} \end{pmatrix}, \tag{8}$$

where each element of the tensor is an expectation value of the electronic wavefunction. It is seen that the tensor is dependent on the selected origin, r_0, and consequently the orientation of the molecule. This dependence is removed by defining an origin invariant second moment tensor, $\widetilde{S}$ [10].

$$\widetilde{S} = \begin{pmatrix} \langle \widetilde{x^2} \rangle & \langle \widetilde{xy} \rangle & \langle \widetilde{xz} \rangle \\ & \langle \widetilde{y^2} \rangle & \langle \widetilde{yz} \rangle \\ & & \langle \widetilde{z^2} \rangle \end{pmatrix}, \tag{9}$$

where

$$\langle \widetilde{ij} \rangle = \langle ij \rangle_{r_a} - \frac{\langle i \rangle_{r_a} \langle j \rangle_{r_a}}{N} \quad i = x, y, \text{ or } z \text{ and } j = x, y \text{ or } z, \tag{10}$$

N is the number of electrons and r_a is an arbitrary origin. The form of $\langle \widetilde{ij} \rangle$ is similar to that seen in a connected moments expansion(CMX) of the energy or some other property of a wavefunction [11]. Also like the second moment tensor of an LMO (Eq. 4), $\widetilde{S}$ can be diagonalized,

$$Q^+ \widetilde{S} Q = \widetilde{S}', \tag{11}$$

$$\widetilde{S}' = \begin{pmatrix} \langle \widetilde{x'^2} \rangle & 0 & 0 \\ & \langle \widetilde{y'^2} \rangle & 0 \\ & & \langle \widetilde{z'^2} \rangle \end{pmatrix}. \qquad (12)$$

The eigenvalues, $\langle \widetilde{x'^2} \rangle$, $\langle \widetilde{y'^2} \rangle$ and $\langle \widetilde{z'^2} \rangle$, correspond to the principal axes of the electronic second moment of the molecule, Q, and can be associated with the major and minor axes of an ellipsoid that describes the shape of the molecule. A quantitative measure of size may be calculated from the eigenvalues, such as the geometric average of the axes,

$$\widetilde{R} = \left(\langle \widetilde{x'^2} \rangle \langle \widetilde{y'^2} \rangle \langle \widetilde{z'^2} \rangle \right)^{1/6} \qquad (13)$$
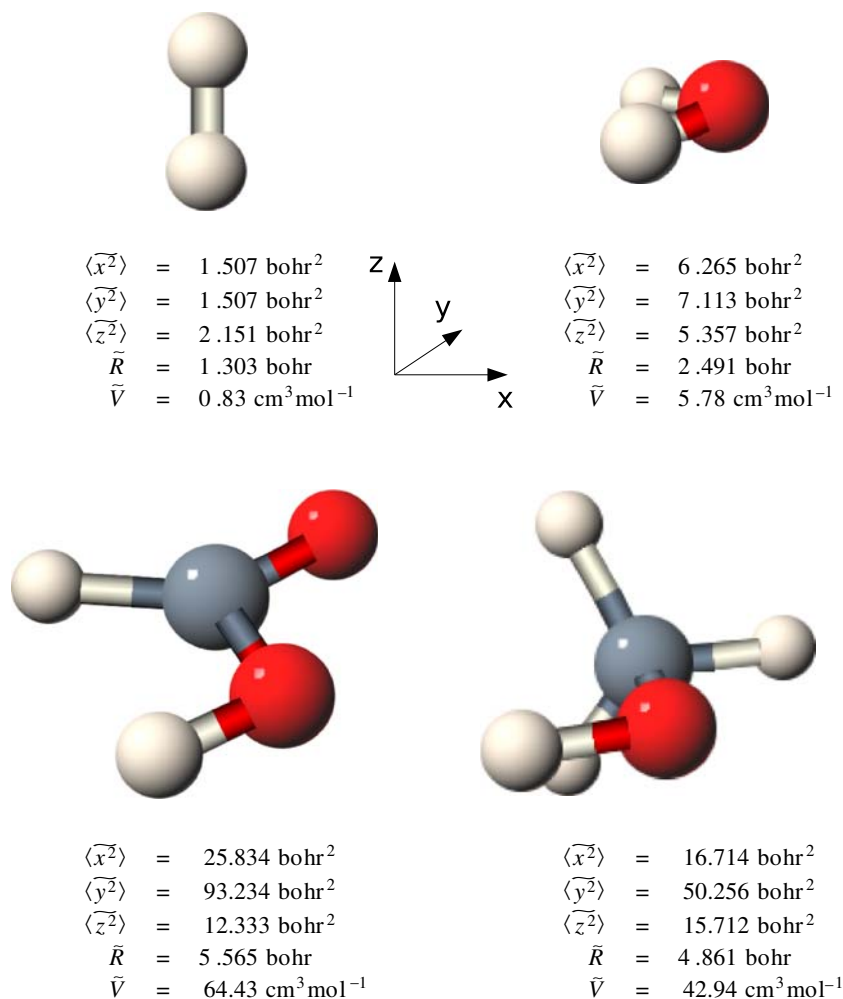
and the molecular volume,

$$\widetilde{V} = \frac{4\pi}{3} \widetilde{R}^3 = \frac{4\pi}{3} \sqrt{\langle \widetilde{x'^2} \rangle \langle \widetilde{y'^2} \rangle \langle \widetilde{z'^2} \rangle}. \qquad (14)$$

The size or volume of a functional group, or substituent, X may be defined as the size or volume of the molecule HX, where the volume of H is taken to be constant.

An illustration of molecular sizes and shapes, calculated at HF/6-31G(d), is given in Fig. 1. As expected the H_2 molecule is larger in the z-direction, 2.151 bohr^2, and symmetric in the xy-plane, 1.507 bohr^2. It is seen that water is largest in the y-direction, 7.113 bohr^2, which corresponds to the OH bonds. For methanol and formic acid, it is seen that both molecules are significantly larger along the y-axis, 50.256 bohr^2 and 93.234 bohr^2 respectively, which is the general direction of their CO bonds. As expected the volume of the molecules increase in the order $H_2 \left(\widetilde{V} = 0.83 \mathrm{cm}^3\mathrm{mol}^{-1} \right)$, $H_2O \left(\widetilde{V} = 5.78 \mathrm{cm}^3\mathrm{mol}^{-1} \right)$, $CH_3OH \left(\widetilde{V} = 42.94 \mathrm{cm}^3\mathrm{mol}^{-1} \right)$, to $CHOOH \left(\widetilde{V} = 64.43 \mathrm{cm}^3\mathrm{mol}^{-1} \right)$.

This origin invariant formulation for the size of a molecule is also found to correlate quite well with another theoretical measure of molecular volume. A significantly more complex method of calculating molecular volume is through use of isodensity contours. During the development of the theory of atoms and molecules, Bader et al. investigated the volume of molecules using isodensity contours [15]. Upon comparing the origin invariant volume, $\widetilde{V}$, to the Bader volume, V_ρ, it is found that $\widetilde{V}$ is smaller

Fig. 1 The shape and size of some small molecules(H_2, H_2O, CH_3OH, and CHOOH) calculated at HF/6-31G(d). Molecules are slightly rotated off the indicated principle axes to show all atoms

$$\begin{aligned} \langle \widetilde{x^2} \rangle &= 1.507 \text{ bohr}^2 \\ \langle \widetilde{y^2} \rangle &= 1.507 \text{ bohr}^2 \\ \langle \widetilde{z^2} \rangle &= 2.151 \text{ bohr}^2 \\ \widetilde{R} &= 1.303 \text{ bohr} \\ \widetilde{V} &= 0.83 \text{ cm}^3\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \langle \widetilde{x^2} \rangle &= 6.265 \text{ bohr}^2 \\ \langle \widetilde{y^2} \rangle &= 7.113 \text{ bohr}^2 \\ \langle \widetilde{z^2} \rangle &= 5.357 \text{ bohr}^2 \\ \widetilde{R} &= 2.491 \text{ bohr} \\ \widetilde{V} &= 5.78 \text{ cm}^3\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \langle \widetilde{x^2} \rangle &= 25.834 \text{ bohr}^2 \\ \langle \widetilde{y^2} \rangle &= 93.234 \text{ bohr}^2 \\ \langle \widetilde{z^2} \rangle &= 12.333 \text{ bohr}^2 \\ \widetilde{R} &= 5.565 \text{ bohr} \\ \widetilde{V} &= 64.43 \text{ cm}^3\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \langle \widetilde{x^2} \rangle &= 16.714 \text{ bohr}^2 \\ \langle \widetilde{y^2} \rangle &= 50.256 \text{ bohr}^2 \\ \langle \widetilde{z^2} \rangle &= 15.712 \text{ bohr}^2 \\ \widetilde{R} &= 4.861 \text{ bohr} \\ \widetilde{V} &= 42.94 \text{ cm}^3\text{mol}^{-1} \end{aligned}$$

than V_ρ for small molecules and significantly larger than V_ρ for larger molecules. This unproportional growth of $\widetilde{V}$ relative to V_ρ is due to the behavior of the second moment operator, r^2 [10]. A linear relationship was found to exist between V_ρ and the geometric average of the principle axes of the origin invariant electronic second moment, $\widetilde{R}$.

The linear relationship,

$$V_\rho = \alpha \widetilde{R}, \tag{15}$$

for a set of 26 molecules and V_ρ values for an isodensity contour of 0.002 a.u. is shown in Fig. 2. The value of α is 5.45 ± 0.15 cm^{3}mol^{-1} bohr^{-1} and $R^2 = 0.982$ [10]. The measure of molecular size using the electronic second moment, $\widetilde{R}$, is comparable to the molecular volume from isodensity contours, V_ρ, yet it is significantly easier to calculate the second moment of a molecule than trace an isodensity contour and calculate its volume.

The theoretical measure of the size of a functional group, $\widetilde{R}$, also correlates quite well with experimental measures of steric hindrance. It was found that $\widetilde{R}$ correctly predicts the trend of P-values of the halogens and hydrogen [10], where P-values are steric factors measured from the rotational barriers of substituted ethanes [13]. Another measure of steric hindrance which is determined from a conformational process is n-value. The free energy of topomerization of a phane system with an intra-annular substituent X, is used to determine the n-value for X [14]. When the available n-values for a set of substituents is compared to their theoretical size, $\widetilde{R}$, the same trend is predicted, with the exception of NO$_2$ [10]. It is expected that the deviation from the observed trend is due to effects other than sterics, such as electronic interaction of the oxygens of NO$_2$ with the aliphatic chain of the phane system.
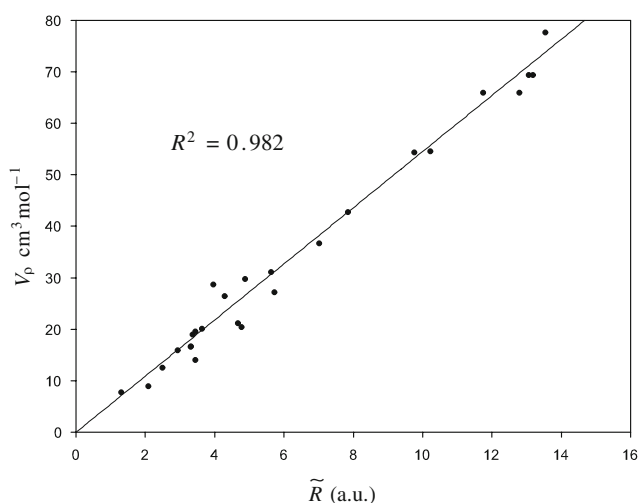
Fig. 2 Comparison of electronic second moment average radius, $\widetilde{R}$(HF/6-31G(d)), to Bader isodensity contour molecular volume [15], V_ρ (ρ=0.002 a.u.). From reference [10]

The theoretical measures of size, $\widetilde{R}$ and $\widetilde{V}$, are easily calculated from the first and second moments of the electronic wavefunction. Another theoretical measure of size, which is substantially more complex, V_ρ, correlates quite well with $\widetilde{R}$. The geometric average of the principle axes, $\widetilde{R}$, is also capable of predicting experimentally measured steric effects. These models of the simple concepts "size" and "shape" are obtained through use of the operators r and r^2, which, at the molecular orbital level, can be used to model interparticle distances.

The *average* interparticle distance

The *average* interelectronic distance

The *average* distance between an electron in MO a and an electron in MO b, is given by [12]

$$(\delta r_{12})_{ab} = \sqrt{\begin{array}{l} \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \\ +\langle y^2 \rangle_a + \langle y^2 \rangle_b - 2\langle y \rangle_a \langle y \rangle_b \\ +\langle z^2 \rangle_a + \langle z^2 \rangle_b - 2\langle z \rangle_a \langle z \rangle_b \end{array}} = \sqrt{\langle ab|r_{12}^2|ab \rangle}, \tag{16}$$

where

$$\langle \mu \rangle_a = \langle a|\mu|a \rangle, \quad \mu = x, y, \text{ or } z. \tag{17}$$

Although this measure is not strictly the expectation value of r_{12} (hence the italicized *average*), it does give a measure of the charge distribution of a single MO, or the interaction between separate MOs. It is important to note that for LMOs, if the electrons occupy the same MO, $a = b$, $(\delta r_{12})_{aa}$ reduces to the definition of the size of an electron pair (Eq. 1), multiplied by $\sqrt{2}$.

$$(\delta r_{12})_{aa} = \sqrt{\begin{array}{l} 2\langle x^2 \rangle_a - 2\langle x \rangle_a^2 \\ +2\langle y^2 \rangle_a - 2\langle y \rangle_a^2 \\ +2\langle z^2 \rangle_a - 2\langle z \rangle_a^2 \end{array}} = \sqrt{2}\|\delta r_a\|, \tag{18}$$

This value is also the root mean square deviation in the position of an electron in MO a, multiplied by $\sqrt{2}$. Unlike the original size of an electron pair (Eq. 1), $(\delta r_{12})_{ab}$ is generalized to pairs of MOs and is applicable to CMOs, as well as LMOs. To illustrate the behavior of such a quantity, the value of $(\delta r_{12})_{aa}$ is calculated for the singlet and triplet states of a series of two-electron systems.

It is seen that for both the singlet and triplet states the distance between the electrons decreases smoothly with increasing nuclear charge, with the exception of the UHF/6-31G triplet systems (Fig. 3). The discrepancy seen is due to the inconsistency of the 6-31G basis set, which for He has
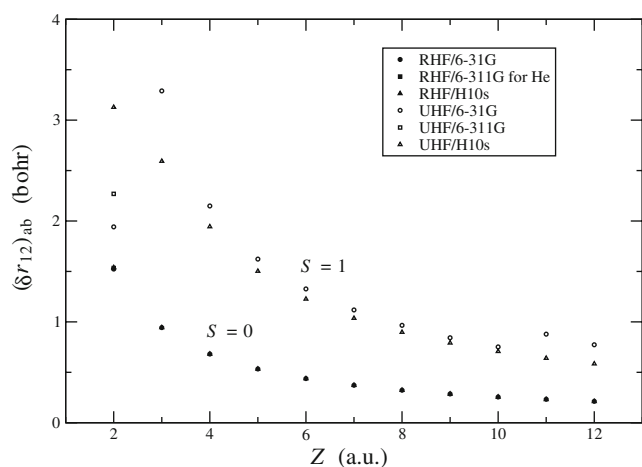
Fig. 3 $(\delta r_{12})_{ab}$ of two-electron singlet and triplet systems with varying nuclear charge(He to Mg^{10+}). Note that some points overlap

Fig. 4 Relationship between Coulomb energy, J_{ab}, and the average distance between two electrons, $(\delta r_{12})_{ab}$, for two-electron ions to molecules with up to 58 electrons(HF/6-31G(d), CMO)

only two s-type functions compared to three s-type functions for the first-row elements. When an extra basis function is added to He, by using the 6-311G basis set, the $(\delta r_{12})_{ab}$ value is increased which agrees more with the trend. A similar effect is seen upon going from Ne^{8+} to Na^{9+}, which is due to the difference in the 6-31G basis set for second and first-row elements. If a Huzinaga basis set with ten s-type functions [16], H10s, is used for all atoms, a much better trend is observed. In the case of the singlet states, it is seen that basis set has little effect on the value of $(\delta r_{12})_{aa}$ of the two-electron systems (Fig. 3). It should also be noted that as expected, $(\delta r_{12})_{ab}^{singlet} < (\delta r_{12})_{ab}^{triplet}$.

$(\delta r_{12})_{ab}$ and the corresponding Coulomb and exchange integrals

Similar to the definition of the size of an LMO, the average distance between electrons is related to a component of the energy, namely the Coulomb energy. One might expect the repulsion between two electrons, J_{ab}, to be inversely proportional to the distance between them, $(\delta r_{12})_{ab}$, which is indeed the case. The Coulomb integral, J_{ab}, is a two-electron integral,

$$J_{ab} = \langle ab|ab \rangle, \tag{19}$$

which is related to $(\delta r_{12})_{ab}$, a property calculated from one-electron expectation values, by the equation

$$J_{ab} \approx \frac{\alpha}{(\delta r_{12})_{ab}}. \tag{20}$$

The relationship between $(\delta r_{12})_{ab}$ and J_{ab} holds for CMOs and LMOs. However, there are significant deviations in the relationship when dealing with delocalized core CMOs (Fig. 4). For example, the $(\delta r_{12})_{ab}$ value for the two lowest energy CMOs of ethane, which involve the cores of
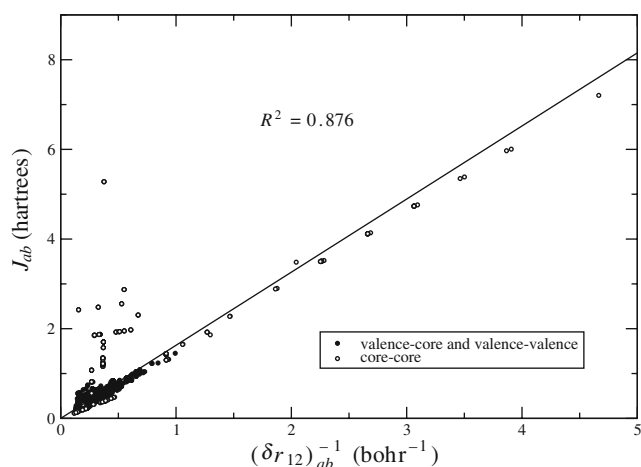
the carbons, is too large and predicts a J_{ab} value that is far lower than the actual HF value. When the molecular orbitals are localized, there are no instances of delocalized cores and the relationship is followed much more closely. The relationship using LMOs for the various systems studied (at HF/6-31G(d)), which includes two-electron ions to 58 electron molecules, has an α (Eq. 20) value of 1.537 ± 0.002 bohrhartrees, and $R^2 = 0.997$ (Fig. 5). Among these molecules are carbon dioxide, propane, acetic acid, hydrogen cyanide, benzene, and uracil. The largest deviation seen in Fig. 4 is actually three points due to the two lowest energy core MOs, 1 and 2, of Cl_2. The value of J_{11}, J_{21} and J_{22} are equivalent as are the corresponding $(\delta r_{12})_{ab}$ values. The underestimation of J_{ab} is due to the large $(\delta r_{12})_{ab}$ value, which is a result of the delocalization of MOs 1 and 2 onto
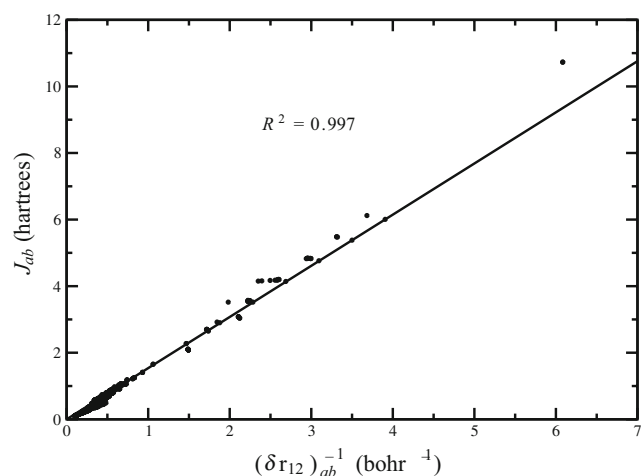
Fig. 5 Relationship between Coulomb energy, J_{ab}, and the average distance between two electrons, $(\delta r_{12})_{ab}$, for two-electron ions to molecules with up to 58 electrons(HF/6-31G(d), LMO)

both chlorine atoms. The internuclear distance, and the lack of MO density between the atoms, leads to an $(\delta r_{12})_{ab}$ value that does not predict the corresponding J_{ab} value. An even larger deviation would be seen for the core MOs of Br_2. The J_{ab} values involving delocalized core MOs could be more accurately modeled using a $(\delta r_{12})_{ab}$ value which is a sum of atomic contributions. For core MOs localized on one atom, or valence MOs over multiple atoms this type of deviation does not occur.

It has also been found, that for simple systems, the exchange integral, K_{ab}, can also be modeled using $(\delta r_{12})_{ab}$.

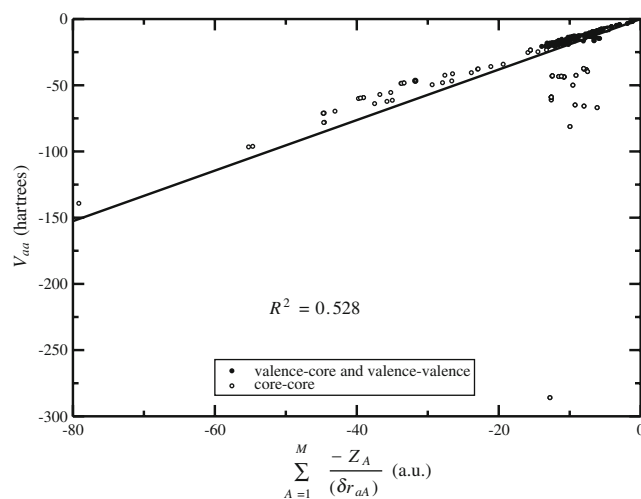$$K_{ab} = \langle ab | ba \rangle, \tag{21}$$

The relationship between K_{ab} and $(\delta r_{12})_{ab}$ for three and four-electron atoms and ions has the same form as the relationship with J_{ab}.

$$K_{ab} \approx \frac{\beta}{(\delta r_{12})_{ab}} \tag{22}$$

There is a slight overlap of the data points in the series of three and four-electron systems (Fig. 6) which is due to the difference in the 6-31G(d) basis set for the first and second-row elements. Despite the uneven basis set, $(\delta r_{12})_{ab}$ models K_{ab} quite well in these systems, with $\beta=$ 0.1193±0.0011 bohrhartrees and R^2=0.998. The ability to model a two-electron property such as the Coulomb or exchange energy with a quantity which is simply calculated from one-electron expectation values is an important result. Calculation of the two-electron integrals which are required for the Coulomb and exchange energies, J_{ab} and K_{ab}, is generally the most time consuming part of an ab initio calculation.

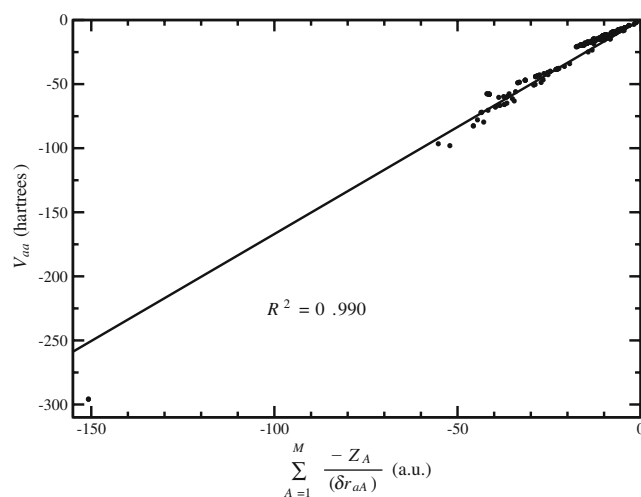

Fig. 7 Relationship between electron-nucleus potential energy, V_{aa}, and the average distance between an electron and a nucleus, δr_{aA}, for two-electron ions to molecules with up to 58 electrons(HF/6-31G(d), CMO)

The *average* electron-nucleus distance and the electron-nucleus potential energy

If the expression for the distance between two electrons, $(\delta r_{12})_{ab}$, is modified by replacing the expectation values of MO b with coordinates of nucleus A, an expression for the *average* distance between an electron in MO a and nucleus A is obtained, δr_{aA}.

$$\delta r_{aA} = \sqrt{\sum_{\mu=x,y,z} \langle a | \mu^2 | a \rangle + \mu_A^2 - 2\langle a | \mu | a \rangle \mu_A} = \sqrt{\langle a | r_{1A}^2 | a \rangle},$$
$$\tag{23}$$

Fig. 6 Relationship between exchange energy, K_{ab}, and the average distance between two electrons, $(\delta r_{12})_{ab}$, for three and four-electron systems with varying nuclear charge(ROHF/6-31G(d))

Fig. 8 Relationship between electron-nucleus potential energy, V_{aa}, and the average distance between an electron and a nucleus, δr_{aA}, for two-electron ions to molecules with up to 58 electrons(HF/6-31G(d), LMO)

where μ_A are the coordinates of nucleus A. As expected there is a relationship between δr_{aA} and the electron-nucleus attraction potential energy associated with an electron in MO a, V_{aa}.

$$V_{aa} = \left\langle a \left| \sum_{A=1}^{M} \frac{-Z_A}{r_{1A}} \right| a \right\rangle \qquad (24)$$

Similar to $(\delta r_{12})_{ab}$ and J_{ab}, the relationship holds for CMOs and LMOs (Figs. 7 and 8), with the exception of the delocalized core CMOs.

$$V_{aa} = \gamma \sum_{A=1}^{M} \frac{-Z_A}{\delta r_{aA}} \qquad (25)$$

The largest deviation seen in Fig. 7 is due the two lowest energy core MOs of Cl_2, as seen with the relationship between J_{ab} with $(\delta r_{12})_{ab}$ (Fig. 4). The electron-nucleus potential energy is calculated from one-electron integrals, therefore modeling V_{aa} with δr_{aA} does not have the same implications as modeling J_{ab} with $(\delta r_{12})_{ab}$. However, the model does demonstrate how, once again, energy components may be modeled using first and second moment operators. These findings, have important consequences. It has been shown that these interparticle distances share an approximate linear relationship with interatomic distance. This result combined with the relationships presented here form a basis for a novel approach to molecular modeling, Simulated electronic structure theory (SEST) [17]. In SEST the energy components associated with individual electrons are expressed as functions of the nuclear coordinates. An empirical model which explicitly includes the electrons has several advantages over conventional molecular mechanics.

Conclusions

Since the theoretical definition of the size of an electron pair was introduced several relationships involving LMO size, energy and stereochemistry have been discovered. However, the idea behind the definition, the use of first and second moment expectation values as a measure of the size of electronic structure, can be further modified for various other purposes. As seen in this study, application of this idea of size to an entire molecule resulted in a theoretical definition of the size of a molecule or functional group. Such a measure, which is origin invariant, is useful for describing chemical structures as well as predicting steric

effects in molecules and reactions. The size of an LMO may be generalized to pairs of MOs, as an expression for the distance between two electrons, $(\delta r_{12})_{ab}$, which also applies to CMOs. Such a property enables the modeling of a complex two-electron property, J_{ab}, using simple one-electron expectation values. The model performs significantly better for LMOs than CMOs. Finally, the formalism of the distance between two electrons can be applied to an electron and a nucleus to give, δr_{aA}. This property is also related to an energy component, the electron-nucleus attraction energy, V_{aa}. Relationships such as these could prove useful in molecular modeling on a larger scale [17]. Furthermore, the success in using first and second moment operators to model the Coulomb and electron-nucleus potential energy, and exchange energy, of a molecule certainly merits investigation into the modeling of other properties, as well as the investigation into higher order moments and their behavior.

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