Bending the Curve: Molecular Manifestations of Electron Antisymmetry

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As very light fermions, electrons are governed by antisymmetric wave functions that lead to exchange integrals in the evaluation of the energy. Here we use the localized representation of orbitals to decompose the electronic energy in a fashion that isolates the enigmatic exchange contributions and characterizes their distinctive control over electron distributions. The key to this completely general analysis is considering the electrons in groups of three, drawing attention to the curvatures of pair potentials, rather than just their amplitudes and slopes. We show that a positive curvature at short distances is essential for the mutual distancing of electrons and a negative curvature at longer distances is essential to account for the influence of lone pairs on bond torsion. Neither curvature is available in the absence of the exchange contributions. Thus, although exchange energies are much shorter range than Coulomb energies, their influence on molecular geometry is profound and readily understood.

Introduction

Chemists have two very different languages for describing molecules, and the subtitle of this paper juxtaposes the two. On the one hand "molecular features" usually references the arrangement of bonds and associated semi-classical electrons. On the other hand, "electron antisymmetry" is only intelligible in terms of electronic wave functions which are typically delocalized across the molecule. Some rapprochement between these two pictures has been achieved by transformations that produce localized wave functions that can be identified with bonding and non-bonding electrons. However, the correspondence is only topological. It begs the question of what energies drive the observed spatial arrangements. On the one hand, the semi-classical picture invokes "valence shell electron pair repulsion" (VSEPR), according to which like-spin electrons avoid each other and unlike-spin electrons form pairs.[1] On the other hand, wave mechanics invokes Coulomb and exchange integrals of the kinetic and electrostatic terms in the Hamiltonian. The purpose of this paper is to bridge these two views and, in particular, to isolate the influences of electron antisymmetry on molecular structures.

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In the next section, we will explore the relationship between energy and particle spacing, noting that the curvature is decisive, independent of magnitudes and slopes. Then we will turn to a choice of localized orbitals that allows analytical evaluation of that relationship. Using this construct, we finally consider which contributions to the energy are able to account for the arrangements of electrons in molecules.

Results and Discussion

Energy Correlates of Particle Spacing

The top row of Figure 1 shows two different spacing scenarios. In both, two identical particles (black) are already in place at a fixed distance. The question is where the third particle will go. In the avoiding (left, red) scenario, the third particle is situated
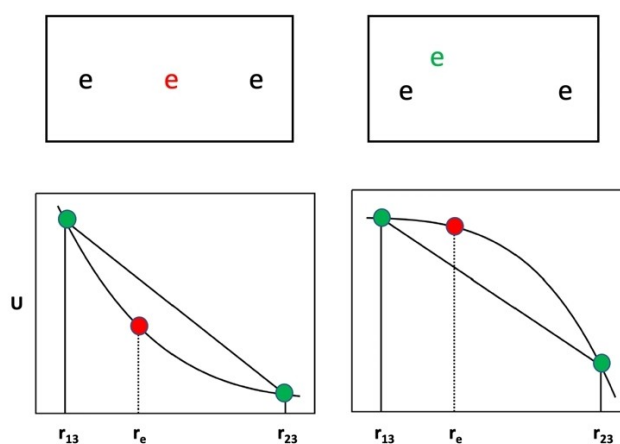
Figure 1. Consequences of negative and positive curvature in pair potentials (see text). The constructs compare $U(r_e)$ (red dot) with $[U(r_{13}) + U(r_{23})]/2$ at the midpoint of the straight line connecting the points on the curve at r_{13} and r_{23} (green dots).

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equidistant from the original two. In the bunching (right, green) scenario, the third particle "prefers" to be closer to one of the original particles than to the other.

The bottom panels in Figure 1 show that which scenario is preferred (i.e., has the lower energy) depends on the curvature of the dependence of the interactions on distance. Suppose that the third electron is set at an equal distance r_e from each of the two original ones. In that case, the red dot represents the average of the repulsion felt by the third electron due to each of the two original ones. Now suppose that the third electron is placed closer to the first electron (r_{13} in Figure 1) and/or farther from the second electron (r_{23} in Figure 1). In that case, the midpoint of the straight line connecting the two green dots represents the average of the repulsion felt by the third electron due to each of the two original ones. When the pair potential has positive curvature (left), the avoiding scenario has the lower energy, and when the pair potential has negative curvature (right), the bunching scenario has the lower energy.

Before moving on to wave functions, it is useful to pause to consider what effect classical interactions would have on electron spacing. As illustrated in Figure 2, classical repulsions between like-charged particles have positive curvature at all distances. According to the above analysis, this means that electrons under this potential would avoid each other to the extent that attractions to nuclei allow. This result, which is independent of spin and mitigates against electron pairing, is the story that wave functions must improve upon.

Localized Orbitals

There are many possible transformations of wavefunctions that leave the physics untouched: as established by the theorems of density functional theory, all that matters (at least for the ground state) is the distribution of the overall electron density. While the details vary according to whether orthogonality is imposed and the choice of the localization criteria and algorithm,[2] localized orbitals typically have nodal surfaces. This
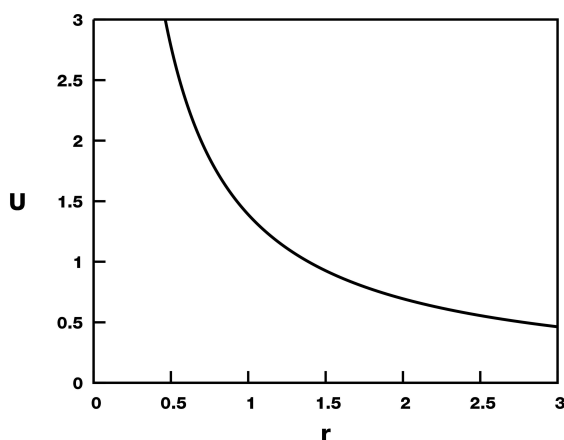
presents both conceptual and practical problems. Conceptually, it is troubling that there is a swath of negligible electron density across a functionally significant region of electron density. The practical issue is the change of sign across the node. It means that contributions to energy integrals, and therefore also to their curvature, change across the node and determining which contributions dominate needs to be delegated to computers.

Recently, Timothy Schmidt et al. have used dynamic Voronoi Metroplis sampling to develop "wave function tiles" which are localized orbitals with no change of sign.[3] Of course, it remains that quantitative evaluation of integrals over these wave functions still needs to be done by computer. However, qualitative features can be extracted by noting that an orbital of a single sign can be represented by a sum of floating spherical Gaussian orbitals (FSGOs):
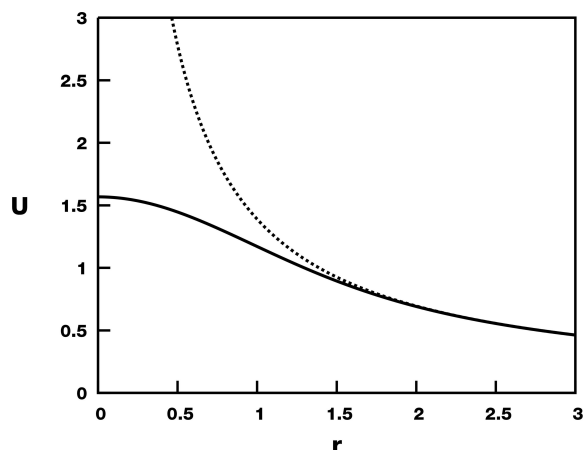
$$\Sigma_i\ C_i\ \exp\ [-(\mathbf{r}\text{-}\mathbf{r}_i)^2/d_i^2],\ \text{all } C_i > 0 \qquad (1)$$

FSGOs have been revisited frequently[4] because they have the advantage of providing analytical integrals over all terms of the Hamiltonian.[5] The practical difficulty is that multiple FSGOs are required to adequately represent molecular orbitals with sufficient quantitative accuracy. However, that is not an impediment to the present qualitative analysis. As long as there are no variations in sign (i.e., all $C_i > 0$ in Equation (1)), each FSGO contributes to a given integral with the same qualitative dependence on the distance between centers, including curvature. Thus, without loss of generality, we can draw qualitative conclusions from the analytical integrals that are available for electrons occupying single FSGOs.[5–6]

Coulomb Integrals

Since the kinetic energy operator is a single electron operator, distance does not enter into the kinetic Coulomb integral. On the other hand, distance does enter into the Coulomb integral for electron-electron repulsions. Figure 3 shows that it differs from the classical repulsion by not diverging at short distances (where the diffuse distribution of the electron density matters). This softened interaction has a characteristic shape, with a negative curvature at short distances and a positive curvature at longer distances (irrespective of electron spin). Each of these features tells an unphysical story. Although mild, the negative curvature at short distances favors bunching of electrons (irrespective of spin), contrary to the observations underlying VSEPR.

At longer, interatomic, distances, the positive curvature of the Coulomb energy favors equal spacing of electrons. Again, this is contrary to what is observed in molecules. Figure 4 shows Newman projections for molecules with various numbers of protons. Proton-proton repulsions are purely Coulombic, with positive curvature everywhere. According to the above analysis, this favors a proton at one end of the molecule being equidistant from the two nearest protons at the other end of the molecule. Thus proton-proton repulsions favor the staggered conformation seen in ethane, methyl amine and meth-

Figure 2. The classical repulsion between a pair of point particles with charge -e, $U = (e^2/4\pi\varepsilon_o)(1/r)$. The energy is plotted in units of $MJ\,mol^{-1}$ vs. r in Å.

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Figure 3. The Coulomb integral for repulsions between two electrons occupying FSGOs with centers separated by a distance r, $U = (e^2/4\pi\varepsilon_o)$ $(2/\pi^{1/2})$ β $F_0(\beta^2 r^2)$ (solid line), is compared with the diverging repulsion between two point charges, $U = (e^2/4\pi\varepsilon_o)(1/r)$ (dotted line). The energies are plotted in units of MJ mol^{-1} vs. r in Å, for $\beta^2 = 2/(d_i^2 + d_j^2) = 1$ Å^{-2}. The Boys function $F_0(x^2) = (\pi^{1/2}/2)(\text{erf}(x)/x)$.[5]
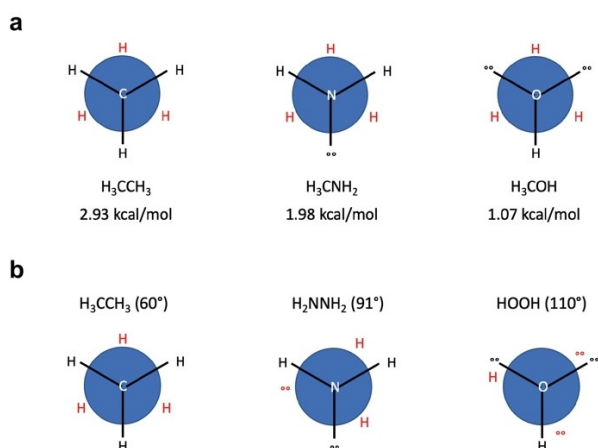

Figure 4. Newman projections of small molecules.[7] (a) For molecules with lone pairs on only one end, there are three torsion barriers of equal magnitude corresponding to conformations where protons at each end of the molecule are eclipsed. (b) In N_2H_4 and H_2O_2, there are two different torsion barriers, a major one at the eclipsed conformation and a lesser one at the staggered conformation, such that the minimum energy structure is skewed. In the stable conformation of H_2O_2, electron pairs at the two ends of the molecule are almost eclipsed, while the two protons still avoid each other.

anol (Figure 4a). Furthermore, this conformation prevails even though the long-range proton-electron attraction has negative curvature. The dominant influence of the proton-proton repulsions is also indicated by the linear decrease in the torsion barrier with the number of protons (Figure 4a). However, in molecules with fewer than three protons on both ends, the staggered conformation is not favored (Figure 4b), indicating that the electron pairs (whether lone pairs or bonding pairs) at one end of the molecule do not prefer to be equidistant from the two nearest ones at the other end.

Exchange Integrals

We now look to the exchange energies to remedy these problems. These energy contributions, arising from exchange integrals over kinetic and electrostatic operators in the Hamiltonian, have been evaluated previously[6] and we make direct use of those results. The integrals are zero for the exchange of localized electrons with unlike spins (as long as the Hamiltonian has no spin-dependent operators).[6] Figure 5 shows contributions for electrons with like spins: at short distances, the magnitudes are 2- to 3-fold less than for the Coulomb integral (solid line in Figure 3) and the damping is sufficiently strong that, as physically required, the exchange interactions are local and do not compete with Coulomb interactions at intermolecular distances. In addition, since the kinetic and electrostatic contributions to the exchange energy are of opposite sign, their magnitudes partially cancel. However, the curvatures are what we are after here and the exchange curvatures are generally of the same sign at short distances, do not fully cancel at longer distances, and are stronger than for the Coulomb interactions.

The contributions to the exchange energy from the kinetic energy operators are positive because the antisymmetric wave function formed by the FSGOs has greater curvature than the corresponding symmetric wave function. Figure 5a shows that this energy depends strongly on the ratio of the cloud sizes
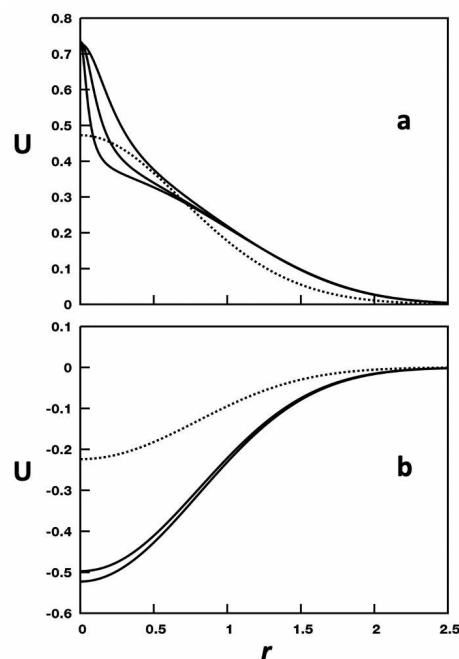
Figure 5. Exchange energies for electrons occupying FSGOs.[6] (a) Contribution to the exchange energy from the kinetic energy operator. $U = (\hbar^2/2m_e)$ β^2 $[3(\gamma^2-1) + \beta^2 r^2]/[\gamma^3 \exp(\beta^2 r^2)-1]$ is plotted in units of MJ mol^{-1} vs. r in Å, for $\beta^2 = 2/(d_i^2 + d_j^2) = 1$ Å^{-2}. $\gamma = [(d_i/d_j) + (d_j/d_i)]/2$ and the solid lines, from left to right, are for $\gamma = 1.001$, 1.005, and 1.02, while the dashed line is for $\gamma = 2$. (b) Contribution to the exchange energy from repulsion between the two exchanged electrons. $U = (-e^2/2\pi^{3/2}\varepsilon_o)$ β $[\gamma - F_0(\beta^2 r^2)]/[\gamma^3 \exp(\beta^2 r^2)-1]$, plotted in units of MJ mol^{-1} vs. r in Å, for $\beta^2 = 2/(d_i^2 + d_j^2) = 1$ Å^{-2}. The Boys function $F_0(x^2) = (\pi^{1/2}/2)(\text{erf}(x)/x)$.[5] $\gamma = [(d_i/d_j) + (d_j/d_i)]/2$ and the solid lines, from bottom to top, are for $\gamma = 1.0$ and 1.05, while the dashed line is for $\gamma = 2$.

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(i.e., the Gaussian decay lengths, d_i and d_j) for the exchanged electrons. However, unless the difference in cloud sizes is extreme, there is a broad region at short range with strong positive curvature (see solid lines). This contribution will therefore favor even distributions of electrons of like spin. Meanwhile, the absence of this contribution for electrons of unlike spin facilitates the formation of electron pairs. The exceptional case in Figure 5a, of negative curvature over the short range (dotted line), is also physically meaningful, allowing electrons of like spin to pile on top of each other if their cloud sizes are sufficiently different. This applies, for example, to the first spin-excited state of two-electron ions in which electrons of like-spin occupy the 1s and 2s orbitals.

The most straightforward electrostatic contribution to the exchange energy, coming from the exchange integral over the operator for the repulsion between the two exchanged electrons, is negative because the antisymmetric wave function formed by the FSGOs has depleted density between the two centers which reduces repulsions. Therefore, this is the exchange contribution that stabilizes high spin states in the Aufbau of ground state electron configurations.[6,8] Figure 5b shows that this energy is not strongly dependent on the relative sizes of the electron clouds, and contributes positive curvature at short range and negative curvature at longer-range. Thus, it contributes to an even spread of like-spin electrons at short range, and promotes skew from staggered dihedral conformations at longer range.

Discussion

According to these results, the implications of exchange energies go beyond typical concerns about the accuracies of calculated molecular energies to the control of fundamental features of molecular structure. This insight, enabled by using FSGOs to represent well-localized molecular orbitals, is obtained with no loss of generality because different shapes of nodeless orbitals can be represented by different sums of FSGOs with the same sorts of energy contributions.

In contrast, conventional, one-off calculations, for different molecules using different methods, do not lend themselves to such generalization. This is especially so for density functional calculations, given the many variations of the exchange and correlation functionals. On the other hand, ab initio results are not friendly to energy decomposition, with varying definitions of such putative structure drivers as "steric interactions" and "Pauli exchange". However, valence bond studies have shown that delocalization is necessary for reproducing torsion barriers at the staggered conformations of N_2H_4 and H_2O_2,[9] and studies of basis set dependence with conventional molecular orbitals have found that torsion barriers are sensitive to the inclusion of polarization and diffuse function.[7,10] These observations agree with our conclusions to the extent that extended orbitals enhance the orbital overlap that is required for the exchange integrals.

Further confirmation of the present attribution of distinct molecular features to exchange energies comes from recent work on sub-atomistic force fields. Sub-atomistic force fields seek to devise potentials for the interactions of semi-classical electrons.[11] The approach is similar to classical molecular mechanics except that electrons are made explicit and independently mobile, with the advantage that polarizability and bond making/breaking are described in a natural, self-consistent and orbital-free manner, without assignment of atom types. In earlier work, we focused on the importance of exchange for stabilizing high spin states, such as the triplet ground states of the oxygen atom and dioxygen.[8] In hindsight, hints of the additional importance of exchange for the distribution of electrons around atoms were present when the heuristically chosen exchange potential had negative curvature at short range: while this potential could account for the ionization and spin excitation energies of monatomic and diatomic species of the 2p elements, overall it produced a very rough potential energy surface with deep local minima for various uneven electron distributions.[8c] Preliminary calculations show that replacing these exchange potentials with ones that have positive curvature at short range provides a smoother potential energy surface. In other work with sub-atomistic force fields, preliminary calculations show that using exchange potentials with negative curvature at interatomic range can predict a torsion barrier at the staggered conformation of N_2H_4.

Conclusion

The VSEPR concept embodies an apparent contradiction: on the one hand, despite "repulsions", electrons are expected to form "pairs", on the other hand "repulsions" cause these "pairs" to distance themselves from one another. The analysis presented in this paper highlights two keys to unraveling this contradiction. One is that what matters for electron spacing is the curvature of the dependence of electron-electron interactions on distance. Thus, while the uniformly positive curvature of repulsions between point particles of like charge disfavors pairing at all distances, the mildly negative curvature of repulsions between diffuse clouds of like charge at short distances allows for pairing. This is true irrespective of spin. The second key to understanding the VSEPR phenomenon is the antisymmetry required of fermion wave functions. The resulting exchange integrals are zero for electrons of unlike spin, but make large contributions to the curvatures of the potentials for electrons of like spin. The attendant positive curvature for electrons of like spin at short distances drives them to even spacing around kernels. On the other hand, at longer distances, the exchange integrals contribute negative curvature that modulates torsion around single bonds.

In sum, our analysis provides readily accessible insights into the important ways that a rather enigmatic feature of the wave properties of electrons manifests in molecular structures. While our thesis is unusually qualitative for a computational chemistry contribution, it is precisely that qualitative nature that affords such general conclusions. We are not aware of any other approach that has been able to develop as broad and yet specific a picture of the influences of the electron exchange

energy on molecular structure and we expect that these insights will influence interpretations of computational chemistry results across methods.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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