Floating Orbitals Reconsidered: The Difference an Imaginary Part Can Make
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ABSTRACT: Floating orbitals for valence electrons have made cameo appearances at several stages in the history of quantum chemistry. Most often, they were considered as potentially useful basis functions and, more recently, also as muses for the development of subatomicistic force fields. To facilitate computation, these orbitals are generally taken to be real spherical Gaussians. However, the computational advantages carry over to complex Gaussians. Here, we explore the potential utility of an imaginary part. Analytical equations for two mobile electrons show that an imaginary part shifts the balance between contributions to the exchange energy that favor parallel versus antiparallel electron spins. However, an imaginary part also carries a large kinetic energy penalty. The imaginary part is therefore negligible for two valence electrons, except in the case of strong core–valence exchange interactions. This consideration allows a self-consistent model for the nd² triplet ground states of transition metal ions versus the ns² singlet ground states of main group ions.

1. INTRODUCTION
Typically, calculations of electronic structure in wave mechanics employ linear combinations of basis functions that are centered on the atoms. Part of the rationale includes our considerable intuition about the roles of various atomic orbitals in bonding. On the other hand, because we also have considerable intuition about electron density in bonding and lone pair regions, the use of "floating" (or "distributed" or "bond") orbitals has frequently been explored on the premise that they can afford more compact and less costly basis sets. However, because it is less straightforward to situate and size such orbitals than to solve for coefficients in large linear combinations of atomic orbitals (LCAOs), the latter approach has generally prevailed.

On a separate track in computational chemistry, Monte Carlo (MC) and molecular dynamics (MD) techniques have been used with atomicistic force fields to simulate atomic trajectories in molecules of ever increasing size. However, these same tools can simultaneously be used to situate and size floating orbitals. In the same spirit, these tools have also been applied to subatomicistic force fields in which valence electrons are modeled as semiclassical particles, a construct that has enabled highly efficient, turnkey simulations of chemical reactions among molecules that are intrinsically flexible and polarizable. In effect, the semiclassical approach assigns valence electrons to floating orbitals with parameters that evolve according to MC or MD protocols. Thus, it seems timely to revisit the floating orbital approach.

Whether atom-centered or floating, orbitals have generally been described with Gaussian functions

$$\psi(x) = \exp\left[-a(r^2 + \zeta^2)\right]$$

for the ease of evaluating the integrals involved in energy calculations (with cusp conditions accommodated by sums of concentric Gaussians in some cases and by distance-dependent corrections in others). Moreover, the employed Gaussians have generally been taken to be real. (The main exception is in ab initio descriptions of resonance states, where it has proven convenient to transform the problem by a rotation of the electron coordinates in the complex plane. When real Gaussians comprise a basis set, the wave functions are complex only to the extent that the coefficients of the linear combinations are complex and each Gaussian contributes to the wave function with a constant phase. In the semiclassical use of floating spherical Gaussian orbitals (FSGOs), there has been no phase variation at all. Here, we consider what may be gained by lifting these severe constraints by allowing the variable a in eq 1 to be complex.

In section 2, we derive the energies of electrons occupying complex FSGOs. In section 3, we explore the simplest, symmetric case of two electrons with a nucleus at the midpoint between them. This makes it easier to identify the unique features that are contributed by the imaginary parts of the orbitals. In particular, we show that the imaginary parts attenuate the contributions to the exchange energy that favor paired spins more strongly than they attenuate contributions that favor unpaired spins. In section 4, we apply these equations to He-like species, the simplest cases that involve exchange integrals. We find that the imaginary parts of the FSGOs turn out to be negligible (close to 0) compared to the real parts, which leads to the result that electron pairing is favored, consistent with the singlet 1s² ground states of these species. In section 5, we consider other ions with just two valence electrons. Here, we first model the shielding

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effects of the core electrons and show that electron pairing is still favored. In section 6, we add a model for the exchange effects of the core electrons and show that this results in an imaginary part of the FSGOs large enough to favor the triplet state. This suggests that the high-spin ground states of transition metals are stabilized by core—valence exchange interactions. Finally, we discuss the implications of these results for developing stabalized by core—valence exchange interactions. Finally, we discuss the implications of these results for developing stabalized by core—valence exchange interactions. Finally, we discuss the implications of these results for developing stabalized by core—valence exchange interactions. Finally, we discuss the implications of these results for developing stabalized by core—valence exchange interactions. Finally, we discuss the implications of these results for developing stabalized by core—valence exchange interactions. Finally, we discuss the implications of these results for develop-

2. ENERGIES OF ELECTRONS OCCUPYING COMPLEX FSGOS

We focus on a two-electron system because that is the simplest that includes the exchange contributions that distinguish the energies for like and unlike electron spins. Given wave functions $\Psi_{\uparrow\downarrow}$ and $\Psi_{\downarrow\uparrow}$, respectively, these energies are

$$U_{\uparrow\downarrow} = \frac{\langle \psi_{\uparrow\downarrow}(1, 2)|H(1, 2)|\psi_{\downarrow\uparrow}(1, 2)\rangle}{\langle \psi_{\uparrow\downarrow}(1, 2)|\psi_{\downarrow\uparrow}(1, 2)\rangle}$$

and

$$U_{\downarrow\uparrow} = \frac{\langle \psi_{\downarrow\uparrow}(1, 2)|H(1, 2)|\psi_{\uparrow\downarrow}(1, 2)\rangle}{\langle \psi_{\downarrow\uparrow}(1, 2)|\psi_{\uparrow\downarrow}(1, 2)\rangle}$$

(2)

where the Hamiltonian includes the quantum kinetic energy of the electrons, the repulsion between the electrons, and the attraction of the electrons to a nucleus $N$ with nuclear charge $Z_N$

$$H(1, 2) = -\frac{\hbar^2}{2m_e}\left[\nabla_1^2 + \nabla_2^2\right] + \frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{r_{12}}\right]$$

$$- \frac{Z_N e^2}{4\pi\varepsilon_0 N} \left[\frac{1}{r_{1N}} + \frac{1}{r_{2N}}\right]$$

and

$$\psi_{\uparrow\downarrow}(1, 2) = \left[\Phi_1(1)\Phi_2(2) - \Phi_2(1)\Phi_1(2)\right]$$

and

$$\psi_{\downarrow\uparrow}(1, 2) = \left[\Phi_1(1)\Phi_2(2)\beta(1)\beta(2) - \Phi_2(1)\Phi_1(2)\beta(1)\beta(2)\right]$$

(5)

respectively, where the spatial orbitals $\Phi_1$ and $\Phi_2$ are FSGOs (eq 1). The forms for electrons with unlike spins (eq 5) fulfill the requirement that the $\alpha$ spin is consistently associated with the electron at position $a$ (top) or position $b$ (bottom), while the $\beta$ spin is consistently associated with the other position. An important consequence is that the exchange integrals for electrons of unlike spins are identically zero due to the orthogonality of spins in the cross-terms. This is physically reasonable given that electrons with unlike spins are not indistinguishable particles. Thus

$$U_{\uparrow\downarrow} = U_{\downarrow\uparrow} + U_{\text{ex}}$$

(6)

where, given the symmetry of the Hamiltonian

$$U_{\uparrow\downarrow} = \frac{\langle \Phi_1(1)\Phi_2(2)|H(1, 2)|\Phi_1(1)\Phi_2(2)\rangle}{\langle \Phi_1(1)\Phi_2(2)|\Phi_1(1)\Phi_2(2)\rangle}$$

$$= \frac{\langle \Phi_1|\Phi_1\rangle}{\langle \Phi_1|\Phi_1\rangle}$$

(7a)

(where we now adopt the conventional compact notation with implicit electrons indices) and

$$U_{\downarrow\uparrow} = \frac{\langle \Phi_2(1)\Phi_1(2)|H(1, 2)|\Phi_2(1)\Phi_1(2)\rangle}{\langle \Phi_2(1)\Phi_1(2)|\Phi_2(1)\Phi_1(2)\rangle}$$

(7b)

The exchange energy is therefore

$$U_{\text{ex}} = U_{\uparrow\downarrow} - U_{\downarrow\uparrow} = \frac{\Delta U}{\Omega}$$

(8)

where

$$\Delta U = \left\{\frac{\langle \Phi_1|\Phi_1|\Phi_2|\Phi_2\rangle}{\langle \Phi_1|\Phi_1\rangle\langle \Phi_2|\Phi_2\rangle} - 1\right\}$$

(9)

and

$$\Omega = \left\{\frac{\langle \Phi_1|\Phi_2\rangle^2}{\langle \Phi_1|\Phi_1\rangle\langle \Phi_2|\Phi_2\rangle}\right\}$$

(10)

Going forward, it is convenient to distinguish between terms arising from the kinetic, repulsive, and attractive parts of the Hamiltonian with the notation

$$U_{\text{k}} = U_k + U_R + U_A$$

$$U_{\text{ex}} = U_{\text{exk}} + U_{\text{exh}} + U_{\text{exh}}$$

(11)

(12)

and

$$\Delta U = \Delta U_k + \Delta U_R + \Delta U_A$$

(13)

indicating a complex conjugate with an asterisk, defining a measure of the inequivalence of $a$ and $b$ as

$$\gamma = \left[\frac{(a^* + b)(a + b^*)}{(a^* + a)(b + b^*)}\right]^{1/2} \geq 1$$

(14)

and making use of Boys’ integrals $^{12}$ defined as

$$F_n(x^2) = \int_0^1 \exp(-x^2t^2)\,t^{2n}\,dt$$

(15)

the energies are given by

$$U_k = \frac{3N^2}{m_e} \left\{\left[\frac{a^*a}{a^* + a} + \left(b + b^* + b\right)\right]\right\}$$

(16)

$$U_k = \frac{e^2}{4\pi\varepsilon_0} \left[\frac{(a^* + a)(b + b^* + b)}{(a^* + a)(b + b^* + b)}\right] \times F_n$$

(17)

$$U_{\text{ex}} = \frac{-Ze^2}{4\pi\varepsilon_0} \left[\left(a^* + a\right)^{1/2}F_n((a^* + a)(\bar{r}_a - \bar{r}_b)^2) + (b + b^* + b)\right]$$

(18)
\( \Omega = \gamma^3 \exp \left( \frac{\left( \frac{a^* b}{a^2 + b^2} \right) + \left( \frac{a b^*}{a^2 + b^2} \right)}{1} \right) - 1 \) \hfill (19)

\[ \Delta U_k = \left( \frac{\hbar^2}{m} \right) \times \left\{ \frac{a^2 + a + \frac{b^2}{a}}{(a^2 + a + \frac{b^2}{a})} \frac{1}{\sqrt{(a^2 + a + b^2)}} \right\} \frac{(a^* + a) + \frac{b^2}{a} b}{a^2 + a + b^2 + \left( \vec{r}_i - \vec{r}_j \right)} \]

\[ \Delta U_k = \frac{\gamma^2}{4 \pi \varepsilon_0 \varepsilon^2} \times \left\{ \frac{(a^* + a) + \frac{b^2}{a} b}{a^2 + a + b^2 + \left( \vec{r}_i - \vec{r}_j \right)} \right\} \]

\[ \Delta U_k = \frac{-Z_N \gamma^2}{4 \pi \varepsilon_0 \varepsilon^2} \times \left\{ \frac{(a^* + a) + \frac{b^2}{a} b}{a^2 + a + b^2 + \left( \vec{r}_i - \vec{r}_j \right)} \right\} \]

\[ \vec{r}_{ij} = \frac{(a^* + a) + \frac{b^2}{a} b}{a^2 + a + b^2 + \left( \vec{r}_i - \vec{r}_j \right)} \] \hfill (23)

The approximation in \ref{eq:32} assumes that the vector between electrons of like spin is essentially orthogonal to the vector from the nucleus to the midpoint between the electrons. This is a reasonable approximation for electrons that are both close to a given nucleus, which are the only pairs that make significant contributions to \( \Delta U_{ij} \) anyway.

For species with one nucleus and just two electrons, it is also expected that the nucleus will be located at the midpoint between the two electrons, as illustrated in \textbf{Figure 1}. In that case reducing the probability of close encounters between the two electrons. For the same reason, \( \Delta U_{ij} \) is positive when the nucleus is in the region between the centers of the two FSGOs, where the electron density is diminished. Of course, when \( a^* = a \) and \( b^* = b \), these results are the same as those obtained previously for FSGOs with no imaginary part.  

3. UNIQUE ROLE OF THE IMAGINARY COMPONENT

In order to explore the difference that an imaginary component of the FSGO can make, it helps to consider the case of

\[ a = b = R + i \Gamma \] \hfill (24)

where \( R \) and \( \Gamma \) are real numbers and \( \gamma = (-1)^{1/2} \). This equality is a reasonable approximation for two electrons in similar environments. Substituting \ref{eq:24} into \ref{eqs:15–22} yields

\[ \gamma = 1 \]

\[ U_k = \left( \frac{3\hbar^2}{m} \right)^{1/2} \left( \frac{3}{R} \right)^{1/2} \left( \frac{3}{\Gamma R} \right)^{1/2} \]

\[ U_k = \left( \frac{3\hbar^2}{m} \right)^{1/2} \left( \frac{3}{R} \right)^{1/2} \left( \frac{3}{\Gamma R} \right)^{1/2} \]

\[ \Omega = \exp \left( \frac{3}{R} \right)^{1/2} \left( \frac{3}{\Gamma R} \right)^{1/2} \left( \vec{r}_i - \vec{r}_j \right)^{1/2} \]

\[ \Delta U_k = \left( \frac{3\hbar^2}{m} \right)^{1/2} \left( \frac{3}{R} \right)^{1/2} \left( \frac{3}{\Gamma R} \right)^{1/2} \]

\[ \Delta U_k = \left( \frac{3\hbar^2}{m} \right)^{1/2} \left( \frac{3}{R} \right)^{1/2} \left( \frac{3}{\Gamma R} \right)^{1/2} \]

Combining \ref{eqs:30, 31, and 33} we find that, when \( \Gamma = 0 \), \( U_{ij} > 0 \) for all \( R \) and \( r \) when \( Z_N = 1 \) (see \textbf{Figure 2a}) and the more so when \( Z_N > 1 \) (because the positive value of \( \Delta U_{ij} \) increases with \( Z_N \)).
As expected, $\Im \neq 0$ adds to the kinetic energy (eq 26) because it increases the curvature of the wave function, whereas it has no effect on the electrostatic energies (eqs 27 and 28) because they depend only on the distribution of electron density. The more interesting results are those for the exchange energy (eqs 29-33). $\Im \neq 0$ has a damping effect via the exponential in $\Omega$ (eq 29). However, this is offset in varying degrees by the exaggerating effect of $\Im \neq 0$ on $\Delta U_{\nu}$, $\Delta U_{\mu}$, and $\Delta U_{\lambda}$ (eqs 30−33). This is especially so for $\Delta U_{\lambda}$ and $\Delta U_{\mu}$ where $\Im \neq 0$ results in terms in which $F_0$ has a negative argument. These terms can be large because, as is evident in eq 15 and illustrated in Figure 3, $F_0(-x)$ becomes exponentially large with increasing $x$. It is also notable that the coefficients for $\Im$ are such that their effect is greater in $\Delta U_{\mu}$ (eq 31) than in $\Delta U_{\lambda}$ (eq 33). Thus, $\Im$ increases the influence of the negative $\Delta U_{\mu}$ which favors like (i.e., unpaired) spins versus the positive ($\Delta U_{\mu} + \Delta U_{\lambda}$) which favors unlike (i.e., paired) spins. The range of $U_{\alpha\alpha} < 0$ when $\Im \neq 0$ is illustrated in Figure 2b,c.

Of course, this influence of $\Im$ is unhelpful for He-like species, which are all $1s^2$ singlets in the ground state. Thus, it is important to examine whether $\Im$ is sufficiently small for these species (as we do in section 4). However, a more interesting application for floating orbitals is the description of valence electrons in heavy elements. Therefore, we go on (in Sections 5 and 6) to consider the influence of core electrons in ions with two valence electrons. Of these, the main group ions have low-spin ground states (e.g., $3d^2$ triplets) consistent with larger values of $\Im$.

### 4. HE AND HE-LIKE IONS

In these two-fold symmetric species, there are three degrees of freedom:

$$r, \, \Im, \, \text{ and } r = |r_e - \vec{r}_N| = |r_e - \vec{R}_N| = \frac{|r_e - \vec{r}_N|}{2}$$

(34)

See eq 24 and Figure 1. We find that the kinetic energy penalty for $\Im \neq 0$ (in eq 26) is sufficiently large that the minimum of $U_{\uparrow\uparrow}(R, \Im, r)$ occurs at $\Im \sim 0$ for all values of $Z_N$. Furthermore, as $U_{\alpha\alpha} > 0$ when $\Im \neq 0$ for all $Z_N$, $\Re$, and $r$, it follows that $U_{\uparrow\downarrow} > U_{\uparrow\uparrow}$ for He and all He-like ions, consistent with the known $1s^2$ singlet ground states of these species.

### 5. INFLUENCE OF CORE ELECTRONS: SHIELDING

A convenient and effective model for the distribution of core electrons is another Gaussian

$$\rho_N(r_e) = \left(\frac{c_N}{\pi}\right)^{3/2} \exp\left[-c_N(r_e - \vec{r}_N)^2\right]$$

(35)

as illustrated in Figure 1.
Although \( U_A \) is highly sensitive to shielding (as illustrated in Figure 4), the shielding effect does not prevent the drive of \( U_{k_k} \) and \( \Delta U_A \) toward large \( \mathcal{F} \) from overwhelming the drive of \( \Delta U_{k_k} \) toward large \( \mathcal{F} \), just as it did across all values of \( Z_N \) in the absence of shielding (in the previous section). Thus, it remains that \( U_{k_k} > 0 \), which dictates a singlet ground state. Comparing the results in Figure 5 with experiment (see abstract graphic), we find that, although the valence FSGO construct greatly overestimates the relative stability of the ns\(^2\) singlet ground states of main group ions, the rising trend with increasing \( Q_N \) is reproduced. On the other hand, the model does not accommodate the nd\(^2\) triplet ground states of transition metal ions.

6. INFLUENCE OF CORE ELECTRONS: CORE–VALENCE EXCHANGE

The above results are obtained without considering energy contributions from valence-core exchange and it may be that valence–core exchange is more important for transition metals where valence electrons are going into a shell that is already partially filled in the core. However, disaggregating the core electrons would greatly diminish the utility of floating orbitals. Therefore, we consider whether the effect of core–valence exchange can be represented by an empirical term in \( U_A \). Given the \((1/\mathcal{F})\) factor shared by all the exchange terms, we expect that core–valence exchange energy should diminish exponentially with distance and with \( \mathcal{F} \) (in Å) for the first two full rows of main group elements with complete shielding (\( \lambda = \epsilon_N^{1/2} = 0.0 \)).

 contracted around the nucleus). The effect is to replace eq 28 with

\[
U_A = \frac{-Z_N e^2}{4\pi\varepsilon_0 r} \left\{ F_0(2\mathcal{R}) \right\} \left( \frac{1}{r_2} \right)\] 

\[
- \frac{Z_N e^2}{4\pi\varepsilon_0 r} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \int \left[ \frac{1}{r_1} + \frac{1}{r_2} \right] \rho(r) \, dr \] 

(36)

and eq 33 by

\[
U_A = \frac{-Z_N e^2}{4\pi\varepsilon_0 r^{1/2}} \left\{ 2F_0 \left( \frac{2\mathcal{R}}{r} \right) \right\} \left( \frac{\mathcal{F}}{2\mathcal{R}} \right) \left( \frac{1}{r} \right) \] 

\[
- F_0(2\mathcal{R}) \left( \frac{1}{r_2} \right) \] 

\[
- \frac{Z_N e^2}{4\pi\varepsilon_0 r^{1/2}} \left\{ 2F_0 \left( \frac{2\mathcal{R}}{r} \right) \right\} \left( \frac{\mathcal{F}}{2\mathcal{R}} \right) \left( \frac{1}{r} \right) \] 

(37)

(38)
In eq 39, the exchange term is proportional to the number of core electrons of a given spin, \((Z_N - Q_N)/2\), and has two scaling constants, \(\chi_N\) and \(\tau_N\), that can depend on the core. In particular, it is hypothesized that \(\chi_N\) is negligible when the core—shells are filled (as for main group elements) and \(\chi_N > 0\) when they are not (as for transition metals). For \(\chi_N > 0\), the core—valence exchange energy clearly favors larger \(\Re\) and larger \((\Im 2/\Re)\), with the latter favoring the triplet state.

Figure 6 shows that the results are strongly dependent on the shielding, with the triplet state favored only when shielding is sufficiently strong (i.e., when the value of \(\lambda = c_0^{-1/2}\) is sufficiently small). Notably, although the magnitude of the stabilization of the triplet is small compared to the experimental values (see abstract graphic), the trend across the transition metals is correct, with greater stabilization of the \([Ar]3d^2\) triplet state for larger \(Z_N\). Given that spherical Gaussians are obviously crude descriptions of the valence orbitals and core electron distribution, the quantitative discrepancy is understandable, whereas the qualitative agreement suggests that attribution of the triplet ground state in \([Ar]3d^2\) ions to core—valence exchange is phenomenologically reasonable.

7. DISCUSSION AND CONCLUSIONS

Our goal has been to identify how the imaginary part of a floating orbital might be useful in describing valence electrons. We find that an imaginary part changes the balance between different contributions to the exchange energy for a pair of electrons such that the bias against the triplet state is reduced. However, due to the large contribution of an imaginary part to the kinetic energy, the imaginary part is generally negligible. This is consistent with the \(1s^2\) singlet ground states of all He-like ions. For more relevant ions, we consider the effect of core electrons on a pair of valence electrons. Initially considering only shielding of the nuclear attraction, we again find that the imaginary part of the floating orbital is negligible. This is consistent with the \(ns^2\) singlet ground states of the ions of the main group elements, including qualitative trends within and between rows but not with the \(nd^2\) triplet ground states of the ions of the transition metals. We hypothesize that the latter reflects core—valence exchange interactions, supposing that this effect is more important when the valence electrons belong to the same shell as the “outmost” core electrons. Choosing a plausible form for the core—valence exchange energy, we find imaginary parts that are sufficiently large to stabilize the triplet state when the shielding is sufficiently strong (i.e., when the core electron density is sufficiently compact). Moreover, the stabilization shows the correct trend, becoming stronger with increasing atomic number. However, the magnitude of the stabilization is small compared to experimental values.

The analytical forms of the energy integrals obtained here rely on the use of spherical Gaussians for valence electron orbitals and core electron densities. As this is a crude approximation, we expect no more than qualitative insight. However, such insights have proved useful in the development of subatomic force fields in which independently mobile valence electrons are modeled as semiclassical particles interacting with each other and with kernels via potentials that take quantum effects into account. For a number of main group elements, studies based on spherical Gaussian orbitals have provided the forms of the potentials implemented in eFF\(^2\) and an interpretation of the potentials discovered heuristically in LEWIS.\(^2\) The present work shows how this approach may be extended to the transition metals. Whereas, the main group elements only require that the valence electrons have four dynamic variables (a set of three Cartesian coordinates and a real cloud size parameter), including the transition metals requires a fifth dynamic variable (an imaginary cloud size parameter). This additional dynamic variable (which is expected to be significant in magnitude only near the kernel of a transition metal) imposes a very modest addition to computational overhead.

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**Conflict of Interest**

The authors declare no competing financial interests.

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