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Symmetry Breaking and Self-Interaction Correction in the Chromium Atom and Dimer

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Density functional approximations to the exchange-correlation energy can often identify strongly-correlated systems and estimate their energetics through energy-minimizing symmetry-breaking. In particular, the binding energy curve of the strongly-correlated chromium dimer is described qualitatively by the local spin density approximation, and almost quantitatively by the PBE generalized gradient approximation, where the symmetry breaking is antiferromagnetic for both. Here we show that a full Perdew-Zunger self-interaction-correction (SIC) to LSDA seems to go too far by creating an unphysical symmetry-broken state, with effectively zero magnetic moment but non-zero spin density on each atom, that lies approximately 4 eV below the antiferromagnetic solution. A similar symmetry-breaking, observed in the atom, corresponds better to the $3d^{\uparrow\uparrow}4s^{\uparrow}3d^{\downarrow\downarrow}4s^{\downarrow}$ configuration than to the standard $3d^{\uparrow\uparrow\uparrow\uparrow\uparrow}4s^{\uparrow}$. For this new solution, the total energy of the dimer at, its observed bond length, is higher than that of the separated atoms. These results can be regarded as qualitative evidence that the SIC needs to be scaled down in many-electron regions.

I. INTRODUCTION

Transition metal physics hosts myriad interesting properties, allowing it to play vital roles in biochemistry, electronics, and energy sciences[1–4]. This makes understanding the energetic properties of transition metal molecules important. However, strong correlations in Cr_2, even decades after the experimental determination of its potential energy curve (PEC) by Casey and Leopold[5], remain a challenge for all but the most expensive correlated-wavefunction methods[6–13].

Most investigations of materials involve using the computationally efficient formalism of density functional theory (DFT)[14,15]. Within this formalism, the ground state energy can be expressed as a functional of the ground state density $\rho(\mathbf{r})$:

$$E = T_s + \int d^3r \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}\left[\rho_\uparrow, \rho_\downarrow\right], \tag{1}$$

where T_s is the non-interacting kinetic energy and $E_{\text{xc}}\left[\rho_\uparrow,\rho_\downarrow\right]$ is the exchange-correlation functional. Although exact in principle, in practice one needs to approximate the many-body effects captured by the exchange-correlation functional $E_{\text{xc}}[\rho_\uparrow,\rho_\downarrow]$. There have been several local, semi-local, and even non-local approximations proposed, however, almost all of them suffer from self-interaction errors (SIEs). SIEs largely limit the accuracy of DFT leading to incorrect descriptions of several properties in molecules as well as solids[16–19]. The effects of these errors are more pronounced in transition metal systems due to the localized nature of the occupied d and f orbitals[18,20]. For example, it has been shown by Harrison that s-d interconfigurational energies and spin-flip energies of transition metal atoms can be greatly improved when self-interaction-corrected functionals are used[21,22]. Withanage *et al* found similar improvements when they looked at the adsorption of small molecules on transition metal ions[23] highlighting the need for including self-interaction corrections (SICs) when studying systems containing occupied d and f shells. A formally correct method to remove one-electron self-interaction errors was proposed by Perdew and Zunger (PZ)[18] where they removed the self-interaction error in an orbital-by-orbital manner (PZ-SIC). PZ proposed but did not apply an energy-minimizing unitary transformation of the occupied Kohn-Sham orbitals to orbitals that are likely to be localized, at least for correction of the local spin density approximation (LSDA) if not for more accurate approximations that appeared after 1981. They however did stress that localized orbitals are needed for size consistency. The recently proposed Fermi-Löwdin orbital

implementation of self-interaction corrections (FLOSIC) guarantees this key feature of size consistency, and for large systems offers greater efficiency than PZ-SIC, which has a more general unitary transformation of the Kohn-Sham orbitals[24–26]. We will briefly review the PZ-SIC and FLOSIC methods in the next section.

The strong correlation effects in the Cr dimer are of both static and dynamic nature[27]. Capturing these correlation effects has been challenging even for sophisticated wavefunction methods, with the gold-standard coupled-cluster methods (CCSD(T)) strongly underbinding the dimer[28]. Density functionals can however sometimes yield quantitatively correct ground-state results by symmetry-breaking wherein "the strong correlations that are present as fluctuations in the exact symmetry-unbroken ground-state wavefunction are frozen in symmetry-broken electron densities or spin densities of approximate DFT"[29,30]. Such symmetry-broken solutions have been reported in both Perdew-Zunger SIC and FLOSIC calculations[31,32].

Figure 1 shows the lowest-energy symmetry-broken (antiferromagnetic) LSDA and PBE binding energy curves for Cr_2 compared with the experimental curve of Casey and Leopold[5]. The calculations involve adding bond-centered functions to the standard NRLMOL basis set[33] which we have confirmed affects the energy of an isolated atom by less than 0.01 eV. LSDA calculations by Delley, Freeman, and Ellis[34] showed that LSDA with symmetry breaking gives a reasonable result for the binding curve of Cr_2, which requires very many Slater determinants in a CI expansion of the correlated wavefunction. Patton, Porezag, and Pederson[35] later showed that PBE with symmetry breaking improved LSDA's PEC. An explanation for these results could be that strong correlations arise from degeneracies and near degeneracies, which often arise from symmetries, and that symmetry breaking can produce the kind of normal correlation that most density functional approximations are designed to handle[29]. While broken-symmetry spin densities are not correct in finite systems, they are clear indicators of strong correlation. The extent to which a good functional plus energy-minimizing symmetry breaking can reliably mimic the energetics of strongly-correlated systems is still unknown, although there are supporting examples including stretched H_2[36,37] and equilibrium C_2[30].

In this work, we present a new and seemingly unphysical symmetry-broken solution in LSDA-FLOSIC for the Chromium dimer, with significantly lower energies than the conventional electronic structure associated with the antiferromagnetic state that has been previously reported[34,35,38,39], to be the density-functional ground state. We tentatively attribute this new solution to the fact that PZ SIC needs to be scaled-down in many-electron regions[40–42]. Initial evidence for this need can be found in the work of Pederson and Lin[43], where the authors found that, while Kohn-Sham exchange-only LSDA makes the total energy less negative than the exact exchange-only total energy, exchange-only

SIC-LSDA makes the total energy more negative than the exact exchange-only total energy, and even more negative than the experimental total energy for atoms heavier than Cl. We now know that LSDA becomes exact in a relative sense for the exchange energies of neutral atoms in the limit of large atomic number, a fact employed by Santra and Perdew to show that full PZ SIC makes a spurious correction to LSDA in a system of uniform electron density.[41].

In the following text, we refer to this unusual atomic state as exhibiting on-atom antiferromagnetic behavior. However, an alternative description is that rather than presenting with a $3d_\uparrow^5 4s_\uparrow^1$ valence it instead exhibits a $3d_\uparrow^2 3d_\downarrow^2 4s_\uparrow^1 4s_\downarrow^1$ valence. The triple spin flip allows the antiparallel 3d electrons to order in a manner that they avoid one another and decrease the total Coulomb energy, e.g. $\frac{1}{2}\int d^3r d^3r' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}$, by more than 100 eV. The on-atom orbital ordering or antiferromagnetic behavior stands out dramatically in Fig. 4a.
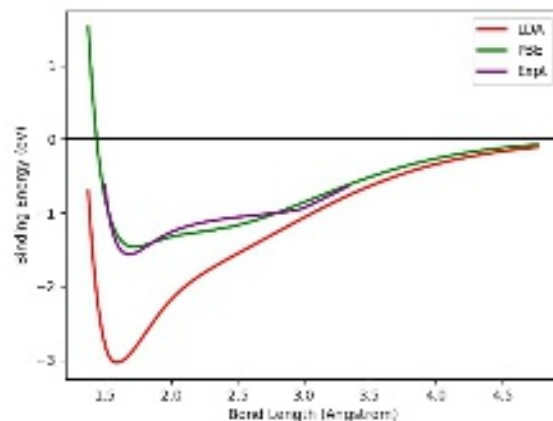

FIG. 1: Comparison of symmetry-broken (antiferromagnetic) LSDA and PBE[44] binding energy curves with the experimental binding energy curve[5] fit to cubic splines.

A. Theory and computational details

In exact DFT, the exchange-correlation energy perfectly cancels the self-Hartree energy for any one-electron density. Local and semilocal functionals clearly cannot display such a cancellation, yielding a residual energy called the self-interaction error. In PZ-SIC, this self-interaction error is removed in an orbital-by-orbital manner[18]

$$E^{\text{DFT-SIC}}[\rho_\uparrow, \rho_\downarrow] = E^{\text{DFT}}[\rho_\uparrow, \rho_\downarrow] \quad (2)$$
$$- \sum_{i\sigma}\{U[\rho_{i\sigma}(r)] + E_{\text{xc}}^{\text{DFT}}[\rho_{i\sigma}(r), 0]\}.$$

In the above equation, the one-electron densities $\rho_{i\sigma}(r)$ are computed from the PZ-SIC orbitals $\{\phi_{i\sigma}\}$ by the expression:

$\rho_{i\sigma}(\mathrm{r}) = |\phi_{i\sigma}(r)|^2$. $U[\rho_{i\sigma}]$ and $E_{xc}[\rho_{i\sigma}, 0]$ are the self-Hartree and approximate exchange-correlation energies respectively.

The single-electron orbitals $\phi_{i\sigma}(\mathrm{r})$ are obtained by solving Schrödinger-like equations with an orbital-dependent potential $v_{\text{eff}}^{i\sigma}(\vec{r})$ given by

$$v_{\text{eff}}^{i\sigma}(\vec{r}) = v_{\text{ext}}(\vec{r}) + \int d^3 r' \frac{\rho(r')}{|\vec{r} - \vec{r}'|} + v_{\text{xc}}^{\sigma}(\vec{r}) - \left\{ \int d^3 r' \frac{\rho_{i\sigma}(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{\text{xc}}^{i\sigma}(\vec{r}) \right\}. \tag{3}$$

Here, the bracketed terms constitute the contributions of the self-interaction correction (FLOSIC) to the standard Kohn-Sham potential.

As mentioned previously, PZ-SIC does not guarantee localized single-electron orbitals which are crucial for a size-consistent theory. The resolution to this size-consistency problem lies in a restriction of the unitary transformations of the occupied Kohn-Sham orbitals. An early implementation of energy-minimizing unitary transformations in PZ-SIC was done by Pederson, Heaton, and Lin[43], although that approach did not guarantee localization and size-consistency. Recently, Pederson, Ruzsinszky, and Perdew formulated an implementation of PZ-SIC that uses localized Fermi-Löwdin orbitals in the PZ-SIC energy functional, which we now call the FLOSIC method[24–26]. Fermi orbitals $F_{i\sigma}(\mathbf{r})$ are constructed from the Kohn-Sham orbitals $\{\psi_{\alpha\sigma}(\mathbf{r})\}$ according to

$$F_{i\sigma}(\mathbf{r}) = \frac{\Sigma_\alpha \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\left\{ \Sigma_\alpha |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2 \right\}}}. \tag{4}$$

In the above expression, the vectors $\mathbf{a}_{i\sigma}$ are called Fermi-orbital descriptors (FODs). The constructed Fermi-orbitals are normalized but not necessarily orthogonal. The Löwdin method[45] is hence applied to the Fermi orbitals to generate a set of orthonormal Fermi-Löwdin orbitals which are then used in the PZ-SIC energy functional. While one usually works with real FLOs (rFLOSIC), by allowing the FODs to take values in the complex plane, one can obtain complex FLOs (cFLOSIC) whose densities are typically less noded than their real counterparts[46]. This leads to reduced energy errors, as it has been established that the evaluation of semi-local functionals on noded one-electron densities limits the accuracy of PZ-SIC[47]. The use of complex orbitals was shown to improve the description of self-interaction corrected ground state properties of atoms[48]. Ivanov. *et al.* emphasized the need for complex-valued functions to obtain accurate results when studying the PEC of Mn_2 using a scaled-down version of PZ-SIC without new symmetry-breaking[49]. Similar improvements in the description of equilibrium properties of *sp* molecules have been observed in the FLOSIC method when complex orbitals were used[47].

Although the aforementioned SIC schemes yield functionals that are one-electron self-interaction-error-free, they often worsen the equilibrium properties when used with semi-local functionals due to an overcorrection[40,50,51] in many-electron like regions. Attempts have thus been made to

scale down the SIC correction. Jónsson and coworkers determined that, for the PBE functional, scaling the SIC by half gave improved results for binding energies and bond lengths of small molecules[52]. Recently, a local scaling of rFLOSIC has been proposed that can be implemented quasi-self-consistently (quasi-LSIC) and has been employed in studies of electron density-related properties such as dipole polarizabilities[42,53,54]. In this work, we report rFLOSIC, cFLOSIC, and quasi-LSIC results for our new symmetry-broken solutions.

The calculations reported in this paper were performed using the UTEP-NRLMOL-based FLOSIC code[25,33,55–58]. All calculations are spin-unrestricted and no symmetry constraints are placed during FOD optimization. The FOD force tolerance is set to 10^{-3} Hartree/Bohr for LSDA-FLOSIC calculations and an energy convergence criterion of 10^{-6} Hartree is chosen for both LSDA-FLOSIC and quasi-LSIC calculations. For calculations involving the dimer, the standard NRL-MOL basis set is supplemented with Gaussians at the bond center.

During the optimization of FODs, one typically encounters several local energy minima[59], making it essential to consider multiple FOD starting points to obtain the true ground state. For the dimer at the equilibrium bondlength, these starting guesses were systematically constructed from a set of previously optimized S=3 atomic FODs in the following manner.

1. Copies of the atomic set of FODs are generated and are rotated/inverted using orthogonal matrices.

2. The spins of the FODs of the copy are flipped.

3. A direction is chosen for the bonding axis and the copy is translated by the PBE-GGA bondlength[35] along this axis to create the starting point for the second atom. Differences between PBE-GGA, the LSDA in the Perdew-Wang parametrization[60], and experimental bondlengths are insignificant from the perspective of this paper.

In this way, a total of 120 starting guesses were constructed (24 orthogonal matrices and 5 axis directions). The presented symmetry-broken solution for the dimer corresponds to the lowest converged LSDA-FLOSIC energy obtained from these guesses. One can construct a good starting point for the symmetry-broken atomic solution from the FODs of the dimer in the stretched-bond (isolated-atom) limit.

II. RESULTS

A. The Dimer

The chromium dimer is formally said to form a sextuple bond with all the valence 3d and 4s electrons participating in the bonding. Past DFT calculations, however, find an antiferromagnetic (AFM) state to be most stable[35,38,61]. In this section, we report Hartree-Fock (HF), LSDA-FLOSIC, and quasi-LSIC results for the AFM state as well as a new symmetry-broken state of the chromium dimer. Unlike the AFM solution, the new solution effectively has a net spin moment of zero on each atom, which is consistent with the sextuple bond picture. For all calculations, the internuclear separation is fixed at the PBE-GGA value[35], and the net spin is evaluated by integrating the spin density in a sphere of radius half the internuclear separation, centered at each atom. The isosurfaces of the spin density and optimized FOD positions for the AFM and new symmetry-broken states can be found in Figs. 2 and 3, respectively. The HF, LSDA-rFLOSIC, and quasi-LSIC energies of both states are reported in Table I. For all quasi-LSIC calculations reported in this section, the wavefunctions and FODs of LSDA-rFLOSIC calculations were used as initial guesses.
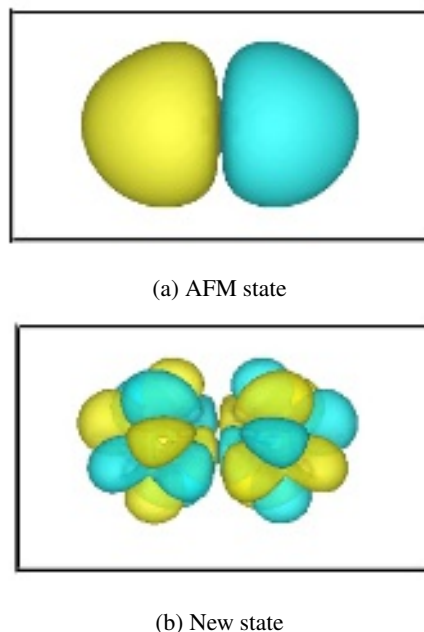

(a) AFM state

(b) New state

FIG. 2: Spin-density isosurfaces of the two symmetry-broken solutions (AFM and new) for the chromium dimer in LSDA-rFLOSIC. Blue/yellow isosurfaces correspond to an isosurface level of ± 0.005 in atomic units. The isosurface for the new state consists of multiple "lobes" indicating strong hybridization of orbitals. Isosurface plots were generated using VESTA[62].

It is interesting to see that LSDA-FLOSIC and quasi-LSIC (with a scaled-down self-interaction correction) qualitatively differ in their predictions for the ground state of the dimer.

While it has been previously reported that quasi-LSIC has a similar performance to its fully self-consistent implementation (including optimization of FOD positions) for smaller atoms[63], we are unsure if this extends to transition metal systems where the energies are typically more sensitive to the FOD positions.
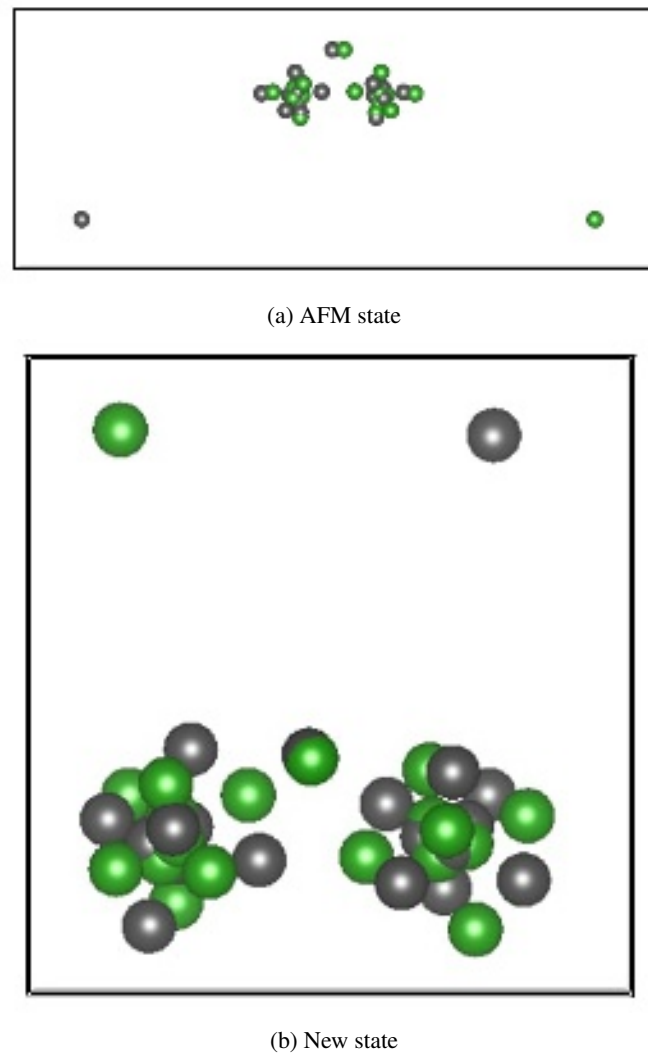

(a) AFM state

(b) New state

FIG. 3: Optimized FOD positions of the two symmetry-broken solutions (AFM and new) for the dimer in LSDA-rFLOSIC. The green/gray spheres depict the 24 spin-up/spin-down FODs. Although no symmetry constraints were placed, the FODs appear to display mirror symmetry about a plane perpendicular to the bond axis passing through the bond center. FODs were visualized using VESTA[62].

An important test for our new symmetry-broken solution is that, at the separated-atom limit, the dimer should reduce to two atoms in the experimental ground state[64]. Surprisingly, we find that this criterion is not met and rather our new solution puts effectively zero net spin on each atom over a broad range of bond lengths, including the dissociation limit. This leads us to a new symmetry-broken singlet state solution for

Functional/method	AFM state	New state	ΔE
	(Y net spin/atom)	(0 net spin/atom)	
LSDA-rFLOSIC	-2092.2053	-2092.3572	4.13
quasi-LSIC	-2088.2841	-2088.2747	-0.25
HF@rFLOSIC	-2086.4156	-2086.1858	-6.25

TABLE I: Energies of the two symmetry-broken states of the dimer evaluated using HF, LSDA-rFLOSIC, and quasi-LSIC. All energies are evaluated at the PBE GGA equilibrium bond length. Y=3.13 for LSDA-rFLOSIC and Y=2.53 for quasi-LSIC (in atomic units). The new solution has a lower energy than the AFM solution in LSDA-rFLOSIC. Total energies are reported in Hartrees. The energy difference (ΔE), defined as E_{AFM}-E_{New}, is reported in eV.

the atom in LSDA-FLOSIC which we now discuss.

The method for finding the nearly spinless, albeit on-atom antiferromagnetic, separated atom limit, is somewhat difficult to explain. Dimer starting points were created by taking two previously determined S=3 atomic starting points, displacing the atoms at $\pm\vec{A}$, such that the bondlength ($|2\vec{A}|$) is the PBE-GGA bondlength, randomly rotating one of the atomic FOD sets about its atom, and then optimizing the group of 48 FODs. Thus, in addition to the diversity offered by different atomic solutions, the starting points depended on a total of five randomly chosen angles. In doing so, the two atoms swapped some of their majority-spin FODS (up for atom A and down for atom B), and effectively yielded two symmetrically identical atoms exhibiting on-atom antiferromagnetic (no net spin on each atom) with lower energy. In other words, we used a 48-electron molecule to find the lowest-energy starting point for two 24-electron atoms that had not earlier been found by considering only the single-atom system. The use of isolated atoms, with higher Z, for finding previously undiscovered solutions for isolated atoms, with lower Z, was recently shown to be useful for demonstrating the existence of solutions in all atoms[65] and the results described here can also be classified in terms of the downward-learning search scheme provided there. We emphasize, as alluded to in other parts of the paper, that these separated-atom-limit solutions may continuously deform into a *completely* unpolarized solution at the equilibrium bondlength, but we have not yet coaxed the molecule into this electronic configuration.

B. The Atom

Studying transition metal systems using the FLOSIC method can be challenging due to the existence of multiple near-degenerate FOD configurations. When investigating optimal FOD positions for atoms, Kao *et al.* determined 5 configurations for the chromium atom corresponding to the lowest LSDA-FLOSIC energy they could find[59]. The spin densities for all those solutions integrated to six unpaired electrons as one expects. As mentioned previously, in this section we report a new symmetry-broken state for the atom in LSDA-FLOSIC with substantially lower energy (-

1046.2161 Hartree) than that previously reported by Kao *et al.* (-1046.1210 Hartree). Our new state contains strongly hybridized atomic orbitals and the net spin density integrates to zero unpaired electrons. PZ-SIC is notorious for "overcorrecting" DFT leading to poor thermochemical accuracy[50,66], and we suspect that the results of this section are an extreme example of this. The FOD positions and spin-density isosurfaces for the symmetry-broken atomic solution are shown in Figure 4. In Table II we report HF, LSDA-rFLOSIC, LSDA-cFLOSIC, and quasi-LSIC energies for the different atomic configurations discussed.

Functional/method	FM state	AFM state	ΔE
	(6 net electron spin)	(0 net electron spin)	
LSDA-rFLOSIC	-1046.1210	-1046.2161	2.58
LSDA-cFLOSIC	-1046.3694	-1046.3766	0.19
quasi-LSIC	-1044.1736	-1044.1120	-1.67
HF@rFLOSIC	-1043.3169	-1043.1814	-3.68

TABLE II: Energies of the different atomic states evaluated using HF, LSDA-rFLOSIC, LSDA-cFLOSIC, and quasi-LSIC. The new AFM solution has a lower energy than the FM solution in LSDA-rFLOSIC, and slightly lower for LSDA-cFLOSIC, however, the cFLOSIC self-consistent results are not yet available so it would be premature to report cohesive energies or to conclude that they will probably not be fixed by cFLOSIC. Total energies are reported in Hartrees. The energy difference (ΔE), defined as E_{FM}-E_{AFM}, is reported in eV.

Similar to what was found for the dimer, LSDA-FLOSIC and quasi-LSIC predict different ground states, whereby the incorrect LSDA-FLOSIC atomic ground state is corrected when a local scaling of the SIC (quasi-LSIC) is considered. This happens for both real and complex FLOs (evaluated here non-self-consistently), although complex FLOs make the two solutions nearly degenerate. We have calculated the Hartree-Fock energies for the two FLOSIC configurations and find that the Hund's rule violation observed with LSDA-FLOSIC is reversed when exact exchange is used.

III. CR$_2$ VERSUS MN$_2$

The idiosyncratic behavior of the Cr$_2$ molecule continues to be a curiosity. Within DFT, Mn$_2$, its neighbor in the periodic table, presents multiple disconnected potential energy curves[67,68] that are individually electronically and magnetically stable with differing local moments, whereas, in Cr$_2$, the local 3d fillings deform uniformly and instead show shoulders in the potential energy curve (PEC). Multiple solutions persist in Mn$_2$ when a globally-scaled-down self-interaction correction is applied[49]. Perhaps understanding why, and if, Mn$_2$ is normal and Cr$_2$ is not will eventually provide another key to this puzzle. We caution that our designation of Mn$_2$ as normal within a DFT picture does not contradict the prevailing view of approximately 30 or more researchers that DFT-based methods predict short bondlength non-vdW-bonded solutions while wavefunction-theory- (WFT) based methods

(a) Side View

(b) Front View
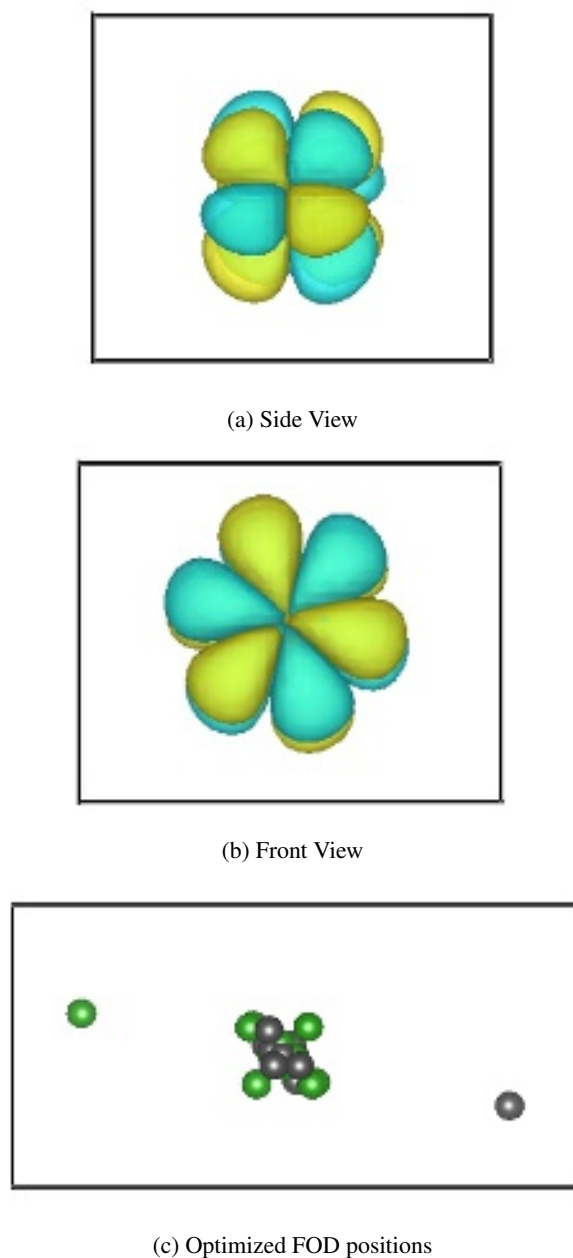

(c) Optimized FOD positions

FIG. 4: Spin density isosurfaces and optimized FOD positions for the new atomic solution in LSDA-rFLOSIC. Figures 4a and 4b show the side and front views of the isosurfaces of the spin density (blue/yellow isosurfaces correspond to isosurface levels of ± 0.005 in atomic units). Fig.4c shows the 24 optimized FOD positions where the green/gray spheres depict the 12 spin-up/spin-down FODs. The FOD visualization and generation of isosurface plots were done using the VESTA software[62].

and possibly DFT-methods can predict higher-energy shallow vibrationally stable vdW minima at larger bondlengths. Ivanov et al.[49] have recently shown that PBE-GGA without self-interaction correction has short-bondlength solutions that persist under a globally scaled-down self-interaction correc-

tion, although the minima of their potential energy curves are shifted above that of a long-bondlength solution, and their bondlengths are increased.

Here, we do not directly address whether the consensus view of Cr_2, Mo_2, and other non-rare-gas atom systems continues to differ from the consensus view of Mn_2. But we re-iterate that the past view on Cr_2[34,39] differed from that on Mo_2, and differs markedly from the WFT-based point of view today[13,27].

In Ref.[69], Dema et al. have reviewed the variable behaviors of the Mn atom in condensed phases which includes three stable bulk phases. This itself points to the possibility that there could be multiple molecular phases that are energetically competitive and potentially difficult to find. We note that in the solid phase, Mn, Cr, and Fe have very similar nearest-neighbor distances, unit-cell structures, and binding energies. We wish to leave open the possibility that everyone that has studied Mn_2 to date has provided computationally accurate results but that the absence of an observed WFT-based short-bondlength solution does not mean it will not eventually be found. We point out further that the experimental *tour-de-force* observation of Mn_2 at low temperatures in rare-gas matrices used ESR spectra [70] to deduce the presence of high-spin Mn dimers and that careful reading of subsequent literature includes speculations that the weak interactions between the rare-gas atoms and the Mn centers were stronger than the Mn-Mn interactions. Experimental observations, based on ESR spectroscopy, of the high-spin long-bond vdW Mn dimer may not rule out the possibility of other potentially lower-energy states of the Mn_2 dimer. We suggest that calculations that study the anisotropy of various Mn_2 solutions and that consider the role of the rare-gas matrices should be considered more deeply before concluding that non-vdW-bonded Mn_2 does not exist. Such a study, while potentially interesting, is beyond the scope and intent of this paper.

Cr_2 is not amenable to analysis with Heisenberg Hamiltonians and, with the possible exception of PBE-GGA, does not yet fit into standard DFT approximations. A simpler system (Ozone) which has pairs of spatially non-orthogonal frontier orbitals with antiparallel spins near the equilibrium geometry has recently been studied with the goal of determining some type of simplified model Hamiltonian[71]. Those techniques may prove useful in future studies of Cr_2, which is very different from a Heisenberg-like molecular magnet such as the Mn_{12}-Acetate[72] molecule. In the latter case, the metal-metal distances are large and the local moments are rigid.

IV. CONCLUSIONS

In this paper, we reported a new LSDA-FLOSIC symmetry-broken solution for the chromium dimer that is consistent with a sextuply-bonded molecule. The spin-density isosurface plot for this new solution (Fig.2) shows multiple "lobes", indicating a strong hybridization of the valence orbitals. Unlike the standard anti-ferromagnetic symmetry-broken solution found without self-interaction correction, our new solution puts essentially zero net spin on each atom over a broad range of

bond lengths, including the dissociation limit. However, we emphasize that there is spin-ordering on each atom which matches Linnett-like chemical pictures[73]. The possible existence of this unusual isolated-atom solution shuld be studied for other transition metal ions.

The standard anti-ferromagnetic solution for the dimer has a physical interpretation[29]: There are dynamic spin-density fluctuations of low frequency that localize up spins on one atom and down spins on the other, and the frequency of these fluctuations tends to zero in the dissociation limit (with six net up spins on one atom and six net down spins on the other). We have no physical interpretation for the new symmetry breaking, and regard it as an unphysical consequence of making a self-interaction correction in many-electron regions where none is needed.

We compared the energy of this new solution with the anti-ferromagnetic state in LSDA-FLOSIC and quasi-LSIC. While LSDA-FLOSIC predicts the new state to be more stable than the AFM state by more than 4 eV, a local scaling of the self-interaction correction qualitatively changes this prediction for the ground state. We note however that the local-scaling approach (quasi-LSIC) is not fully self-consistent, and the results may differ from calculations where relaxation of FODs is allowed. An analogous form of symmetry-breaking was found in the chromium atom. In an extreme example of "overcorrection" in PZ-SIC, FLOSIC incorrectly predicts a broken spin-symmetry singlet-like ground state for the atom. This description is corrected by quasi-LSIC, which might support a need for a local scaling of the self-interaction correction. For the Cr atom, we have ascertained that Kohn-Sham exchange-only, exact Hartree-Fock, and most density-functional approximations give the correct atomic ground-state but that any combination of FLOSIC with LDA-exchange, LDA-correlation or LDA-exchange-correlation, or even the self-interaction corrected Hartree approximation, gives the wrong ordering for the real FODs that we have found. An interesting attribute of the Cr atom is that at the Hartree level, the $d^4 s^2$ orbitally ordered configuration allows the spin-up and spin-down d-electrons to spatially separate and changes the mutual Coulomb energy by 4.2 Hartrees a number that is large compared to the self-interaction energy of valence electrons.

While a self-consistent version of LSIC has been developed [42], it is not yet publicly available. Ref. [42] found that, for sp-bonded systems, self-consistent LSIC was well approximated by evaluating LSIC on the LSDA-FLOSIC occupied orbitals, but our work suggests that this may not be so for the chromium dimer and atom. A fully self-consistent version of cFLOSIC is also not yet available. Presently the lowest complex $d^5 s^1$ atomic solution is only 0.2 eV higher than the orbital ordered $d^4 s^2$ atom and it is possibly reasonable to expect that when a fully self-consistent calculation exists that the high-spin separated atom will indeed be properly accounted for. It is less likely that the high-spin separated atom limit will form a competitive ground-state solution for the molecule because it is known experimentally as well as from standard PBE-GGA calculations[44] that there is a shoulder in the molecular potential energy curve which means a lower-moment Cr_2-structure must cross the high-moment Cr_2

structure at some point. This work raises many new questions about the Cr_2 molecule. While the intricate details of the exact Cr_2 potential energy curve of Fig.1 are probably beyond the reach of density functional approximations, we speculate that it will be possible to find a qualitatively correct potential energy curve from improved self-interaction corrections to symmetry-broken density functional approximations.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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