Spin Signature of Nonlocal Correlation Binding in Metal-Organic Frameworks

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We develop a proper nonempirical spin-density formalism for the van der Waals density functional (vdW-DF) method. We show that this generalization, termed svdW-DF, is firmly rooted in the single-particle nature of exchange and we test it on a range of spin systems. We investigate in detail the role of spin in the nonlocal correlation driven adsorption of H_2 and CO_2 in the linear magnets Mn-MOF74, Fe-MOF74, Co-MOF74, and Ni-MOF74. In all cases, we find that spin plays a significant role during the adsorption process despite the general weakness of the molecular-magnetic responses. The case of CO_2 adsorption in Ni-MOF74 is particularly interesting, as the inclusion of spin effects results in an increased attraction, opposite to what the diamagnetic nature of CO_2 would suggest. We explain this counterintuitive result, tracking the behavior to a coincidental hybridization of the O p states with the Ni d states in the down-spin channel. More generally, by providing insight on nonlocal correlation in concert with spin effects, our nonempirical svdW-DF method opens the door for a deeper understanding of weak nonlocal magnetic interactions.

The modular building-block nature of metal-organic frameworks (MOFs) and their extraordinary affinity for adsorption of small molecules make these nanoporous materials ideal for technologically important applications. MOFs are used, for example, for gas storage and sequestration [1–5], catalysis [6,7], polymerization [8,9], luminescence [10,11], nonlinear optics [12], magnetic networks [13], targeted drug delivery [14], multiferroics [15–17], and sensing [18–21]. The design of novel MOFs with improved properties requires insight into the molecule-MOF interaction. The large unit cells and periodic nature of MOFs make density functional theory (DFT) the prospective tool for a theory exploration. However, both the adsorbate molecule and the MOF's metal centers can carry spin, giving rise to complex magnetic interactions and a molecular-spin response. It is thus crucial that DFT can reliably capture van der Waals (vdW) forces—which govern adsorption in MOFs—in concert with spin effects.

Concerning the former, the last decade witnessed the development of DFT descriptions for these forces [22]. Here, the vdW-DF versions [23–26] stand out by being nonempirical exchange-correlation functionals that are systematic and truly nonlocal extensions beyond the local density approximation (LDA) [27] and generalized gradient approximation (GGA) [28] in the electron-gas tradition [22,29,30]. Subsequent developments include variants which differ by their choice of the semilocal exchange [31–35] and related nonlocal correlation functionals that rely on optimizing parameters [36–38]. The vdW-DF method and relatives have been successfully applied to

numerous materials in general [22,29,39], and to small-molecule adsorption in MOFs in particular [4,5,40–46].

Concerning the spin effects, however, a systematic description within the vdW-DF framework is still missing. Such effects can play important roles not only in MOFs, but in many systems, as Hund's rules reflect a preference for spin-polarized ground states. For example, spin and vdW effects are essential in organic spintronics [47], dimer binding in excited states [48], overlayer formation on magnetic substrates [49], and correctly assessing formation energies [50]. While the nonlocal functional VV09 considers spin in its own way [51,52], there have so far only been pragmatic approaches for vdW-DF—ignoring the effect of spin on the nonlocal correlation altogether [54] or estimating the effect [55–57] using the semilocal correlation of PBE [28].

In this Letter, we formulate a proper extension of vdW-DF to spin-polarized systems, termed svdW-DF, following the design logic of the original functional. We apply svdW-DF to study the nonlocal correlation driven adsorption of H_2 and CO_2 in MOF74 and find that spin plays a significant role, providing a detailed analysis of spin signatures in such vdW bonding. Beyond MOFs, we envision that svdW-DF will lead to wider materials-theory progress in a stimulating role like that of LSDA, i.e., LDA's spin extension [27]. LSDA was introduced to describe bulk-cohesive and molecular-binding energies [50,58,59] but also led DFT to important successes in the study of magnetism [60]. The svdW-DF formulation enables a robust exploration of systems where spin and nonlocal correlations are both important and it makes vdW-DF a general purpose method [61].

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To design svdW-DF as the natural extension of vdW-DF to spin-polarized systems, we revisit the derivation of its nonlocal correlation energy functional. The starting point is the adiabatic-connection formula (ACF) expressed in terms of a scalar dielectric function ϵ that reflects a formal average of the coupling-constant integration over the screened density-response function [23,58,62,63]. This provides a split-up of the total exchange-correlation energy into a nonlocal and semilocal piece $E_{xc}^{\text{vdW-DF}} = E_c^{\text{nl}} + E_{xc}^{\text{int}}$, defined by Refs. [22,23,25,30] in terms of the Coulomb Green's function G and an integral over the imaginary frequency u:

$$E_c^{\text{nl}}[n] = \int_0^\infty \frac{du}{2\pi} \text{Tr}[\ln(\boldsymbol{\nabla}\epsilon \cdot \boldsymbol{\nabla}G) - \ln\epsilon], \qquad (1)$$

$$E_{xc}^{\text{int}}[n] = \int_0^\infty \frac{du}{2\pi} \text{Tr} \ln\epsilon - E_{\text{self}}. \qquad (2)$$

The general-geometry vdW-DF versions [23,25,26] expand the nonlocal correlation energy (1) in terms of a semilocal response function $S \equiv \ln\epsilon$ that is parametrized via the choice of internal semilocal (GGA-type) functional E_{xc}^{int} (2).

To obtain a computationally tractable approximation for E_c^{nl} [22,23,25], vdW-DF relies on a plasmon-pole approximation of S defined in plane-wave representation as $S_{\mathbf{q},\mathbf{q}'} = \frac{1}{2}\bar{S}_{\mathbf{q},\mathbf{q}'} + \frac{1}{2}\bar{S}_{-\mathbf{q}',-\mathbf{q}}$, with

$$\bar{S}_{\mathbf{q},\mathbf{q}'} = \int d\mathbf{r} e^{-i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{r}} \frac{4\pi e^2 n(\mathbf{r})/m}{[\omega_q(\mathbf{r})+\omega][\omega_{q'}(\mathbf{r})-\omega]}. \qquad (3)$$

Here, $n(\mathbf{r})$ is the total electron density and $\omega_q(\mathbf{r})$ is the effective local plasmon dispersion, parametrized by an effective response parameter in the form of an inverse length scale $q_0(\mathbf{r}) = q_0[n] = q_0(n(\mathbf{r}), \boldsymbol{\nabla}n(\mathbf{r}))$; m and e are the electronic mass and charge. The link between the energy per particle of the internal functional $\varepsilon_{xc}^{\text{int}}(\mathbf{r})$ and $\omega_q(\mathbf{r})$ [22,23,30] follows from combining Eqs. (2) and (3) together with a plasmon dispersion $\omega_q(\mathbf{r}) = q^2/2h(q/q_0(\mathbf{r}))$ with a Gaussian shape of $h(x) = 1 - \exp(-\gamma x^2)$, where γ is an arbitrary constant set to $4\pi/9$. Expanding Eq. (1) to second order in S, one arrives at the well-known six-dimensional integral over a universal kernel $\Phi_0(a,b)$

$$E_c^{\text{nl}} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r})\Phi_0(q_0(\mathbf{r})|\mathbf{r}-\mathbf{r}'|, q_0(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|)n(\mathbf{r}'),$$

$$\qquad (4)$$

which defines the approximation for E_c^{nl} [23]. The total exchange-correlation energy $E_{xc}^{\text{vdW-DF}}$ also consists of the semilocal functional E_{xc}^{int} (2). This is, in practice, approximated as $E_{xc}^{\text{int}} \approx E_{xc}^0 = E_x^{\text{GGA}} + E_c^{\text{LDA}}$, based on a number of criteria [23,25,26,31,32,35] and differing from the internal functional E_{xc}^{int} to varying degrees.

The extension of the semilocal part E_{xc}^0 to spin-polarized systems is straightforward. It is given by the exact spin scaling of exchange [64], i.e., $E_x[n_\uparrow, n_\downarrow] = E_x[2n_\uparrow]/2 + E_x[2n_\downarrow]/2$, and the well-established spin dependence of the local correlation [27]. Here $n_\uparrow$ and $n_\downarrow$ denote the spin-density components. Crucially, by applying the very same criteria, we obtain a fully consistent extension of E_c^{nl} for the spin case.

The spin scaling of exchange results in a spin-dependent semilocal response S in Eq. (3), with spin entering exclusively in the denominator through $\omega_q(\mathbf{r})$. The numerator is given by the f-sum rule, specified as the classical plasmon frequency which depends only on the total electron density $n(\mathbf{r})$. The formulation of svdW-DF can therefore be based on a universal-kernel evaluation using the exact same function $\Phi_0(a,b)$ as in vdW-DF. Nevertheless, the form of the effective response parameter q_0—which acts as a scaling parameter in the arguments of Φ_0—must be adjusted, $q_0[n] \rightarrow \tilde{q}_0[n_\uparrow, n_\downarrow]$, to reflect the explicit spin dependence of the plasmon dispersion.

Motivating our procedure for extending the original vdW-DF formulations to a spin-polarized system is the interpretation of the vdW-DF nonlocal correlation energy as a formal summation of zero-point energy shifts [30,65,66]. The vdW-DF framework starts with a description of the semilocal exchange-correlation holes corresponding to the internal functional E_{xc}^{int} [22,25,29], using a plasmon model to characterize the associated response. The vdW-DF nonlocal correlation energy (1) is a rigorous summation of the plasmon-pole shifts that result when such holes couple electrodynamically [30]. Spin clearly affects the GGA-type internal hole, and our svdW-DF formalism represents a proper implementation of how such semilocal spin effects impact the summation of zero-point energy shifts in Eq. (1).

To establish the updated form of $\tilde{q}_0[n_\uparrow, n_\downarrow]$ it is instructive to first revisit how $q_0[n]$ is specified in the spin-neutral case, where it is given as scaling of the Fermi wave vector $k_F(\mathbf{r}) = (3\pi^2 n)^{1/3}$ as follows:

$$q_0(\mathbf{r}) = \frac{\varepsilon_{xc}^{\text{int}}(\mathbf{r})}{\varepsilon_x^{\text{LDA}}(\mathbf{r})} k_F(\mathbf{r}) \equiv q_{0c}[n] + q_{0x}[n], \qquad (5)$$

$$q_{0c}[n] = -\frac{4\pi}{3e^2} \varepsilon_c^{\text{LDA}}, \qquad (6)$$

$$q_{0x}[n] = -\left(1 - \frac{Z_{ab}}{9} s^2\right) \frac{4\pi}{3e^2} \varepsilon_x^{\text{LDA}}. \qquad (7)$$

Here $\varepsilon_x^{\text{LDA}} = -3e^2 k_F/4\pi$ and the exchange gradient corrections are expressed in terms of the scaled gradient $s = |\boldsymbol{\nabla}n|/2k_F n$. These relations (5)–(7) can be directly adapted to the spin case. The correlation part $\tilde{q}_{0c}[n_\uparrow, n_\downarrow]$ is specified by the spin-dependent PW92 LDA correlation energy per particle $\varepsilon_c^{\text{LDA}}$ [27]. For the exchange part

$\tilde{q}_{0x}[n_\uparrow, n_\downarrow]$, the spin-scaling relation [64] gives the following form:

$$\tilde{q}_{0x}[n_\uparrow, n_\downarrow] = \frac{n_\uparrow}{n_\uparrow + n_\downarrow} q_{0x}[2n_\uparrow] + \frac{n_\downarrow}{n_\uparrow + n_\downarrow} q_{0x}[2n_\downarrow]. \quad (8)$$

These equations fully specify the nonlocal correlation energy of svdW-DF. We make svdW-DF self-consistent, implemented in QUANTUM ESPRESSO [67], by computing the corresponding exchange-correlation potential [24]. Further details on the implementation and calculations are provided in the Supplemental Material [68].

We test svdW-DF on three cases of increasing complexity; results are summarized here and details are in the Supplemental Material [68]. For our test cases we use the implementations svdW-DF1 [23] and svdW-DF2 [25] (which are better suited for small molecules) as well as svdW-DF-cx [26] (which is better suited for larger, extended systems). We start with the Li dimer in its triplet state $^3\Sigma$—an ideal test case that critically balances vdW and spin effects. We find a dissociation energy of 53 meV for svdW-DF1 and 70 meV for svdW-DF-cx, the former in good agreement with the experimental value of 41 meV [80]; VV10 and PBE find 77 meV. A second case is given by atomization energies for molecules from the G1 set [81], where spin enters through magnetic molecular ground states and the isolated atoms. We find a mean absolute percentage error of 4.59% and 7.75% for svdW-DF1 and svdW-DF-cx; VV10 and PBE find 5.14% and 7.11%, respectively. For a third, extended-system test, we study the weak chemisorption of graphene on Ni(111) [82–84], finding a binding separation for svdW-DF-cx of 2.12 Å, in excellent agreement with experiment (2.11 ± 0.07 Å [82]). In contrast, svdW-DF1 finds 3.76 Å, VV10 finds 3.37 Å, and PBE essentially does not bind—unlike svdW-DF-cx they all miss a significant chemical component to the binding.

TABLE I. Binding energies in meV of small molecules in the system $\mathcal{M}$-MOF74 + $\mathcal{A}$ with $\mathcal{M} =$ Mn, Fe, Co, and Ni and $\mathcal{A} =$ H$_2$ and CO$_2$. In number triplets the first number refers to the bare binding energy ΔE, the second one includes the zero-point correction ΔE_{ZPE}, and the third refers to the binding enthalpy at room temperature ΔH_{298}.

$\mathcal{M}$	$\mathcal{A}$	Exp.	No spin	Spin
Mn	H$_2$	91 [85]	−473|−524|−524	−133|−117|−117
Fe	H$_2$	104 [86]	−134|−137|−137	−122|−124|−124
Co	H$_2$	111 [85]	−177|−181|−181	−111|−117|−117
Ni	H$_2$	134 [85]	−134|−137|−137	−131|−133|−133
Mn	CO$_2$	331 [87]	−528|−551|−550	−337|−345|−344
Fe	CO$_2$	352 [86]	−344|−353|−351	−315|−323|−321
Co	CO$_2$	383 [88]	−377|−387|−385	−350|−359|−357
Ni	CO$_2$	394 [89]	−300|−311|−309	−377|−390|−387

Table I summarizes the main point of this Letter: that svdW-DF provides insight on the nature of nonlocal spin effects in the adsorption of H$_2$ and CO$_2$ in the linear magnets Mn-MOF74, Fe-MOF74, Co-MOF74, and Ni-MOF74 [90]. The table reports raw svdW-DF binding energies ΔE, as well as values ΔE_{ZPE} corrected for zero-point vibrations of the adsorbates and binding enthalpies at room temperature ΔH_{298}. We note that the adhesion comes entirely from E_c^{nl}—without nonlocal correlations, CO$_2$ would not bind at all and H$_2$ would only bind with a binding energy of ~5 meV.

Overall, we find very good agreement with experiment, which we partly attribute to the cx version of svdW-DF; agreement with other vdW-DF calculations is also good [5]. In all cases we find that the inclusion of spin has an important effect on the binding. Note that the case of Mn is somewhat artificial and the "no-spin" numbers seem inflated—this is a result of the fact that Mn-MOF74 itself requires spin for a proper description of its structure.

Of particular interest is the binding of CO$_2$ in Ni-MOF74, where spin effects play a tantalizing and unexpected role. The CO$_2$ molecule is diamagnetic and should experience a slight repulsion and weaker binding in the presence of the magnetic dipole of Ni—similarly to what is observed in all the other cases in Table I. However, on the contrary, when spin effects are included the binding increases and the molecule experiences a stronger attraction, which warrants further investigation. In the upper panels of Fig. 1 we plot the induced charge density, i.e., the
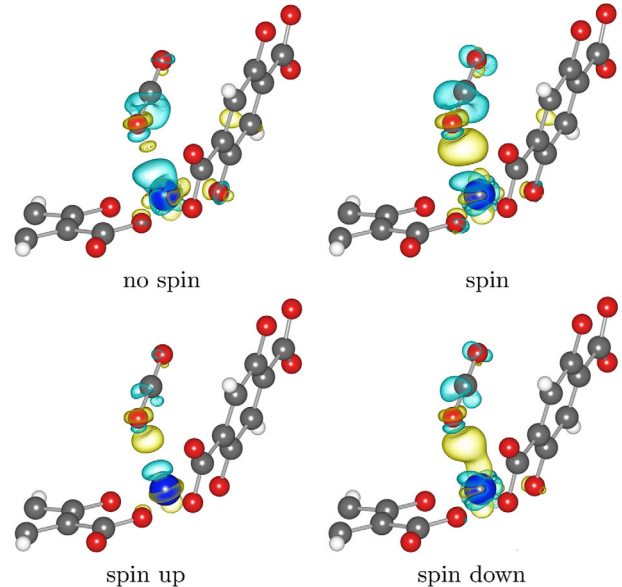

FIG. 1 (color online). Upper panels: Induced charge density upon CO$_2$ adsorption in Ni-MOF74. Lower panels: Induced charge density split into its up and down contribution. Blue (yellow) areas show charge depletion (accumulation). Iso levels are 0.001 e/Bohr^3. See Fig. S1 in the Supplemental Material for the structure of the MOF [68].
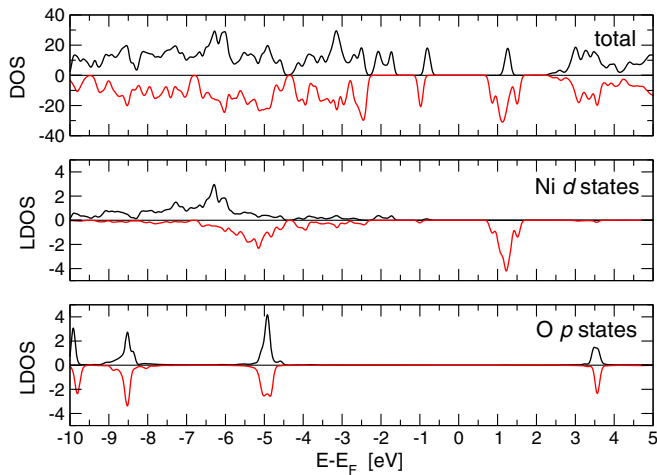
FIG. 2 (color online).   Up (black) and down (red) total density of states (top) and projected density of states on the Ni d states (middle) and O p states (bottom) of the Ni-MOF74 $+ CO_2$ system.

charge density redistribution due to the formation of the bond. It is clearly visible that in the spin case more charge is pulled in between the CO_2 and the metal site, resulting in the stronger binding. In the spin case, we can split this induced charge density further into spin-up and spin-down contributions, as shown in the lower panels of Fig. 1. Here we see the true spin effect: much more spin-down density is being pulled into the bond, compared to spin-up density. This peculiar behavior can be understood by analyzing the projected density of states in Fig. 2. In particular, from the middle and bottom panel we see that at -5 eV the O p states show similar peaks in the spin-up and down channels. However, the projected Ni d states at that point have a large spin-down density while the spin-up density is much smaller. Thus, the O p states hybridize with the Ni spin-down d states, while the hybridization with the spin-up states is negligible (see Fig. S2 in the Supplemental Material for plots of the corresponding orbitals [68]). The interaction of the O p states with the down-spin Ni d states is therefore responsible for the increased and counterintuitive strength of the bond.

As mentioned above, E_c^{nl} is responsible for the entire binding of the small molecules. As such, it is at least indirectly responsible for all the effects we see in our figures and tables. To examine the spin effect of E_c^{nl} explicitly, we also calculate the difference between the binding-induced density of a full svdW-DF calculation and the same calculation without the E_c^{nl} term (Fig. S3, Supplemental Material [68]). Although overall smaller in magnitude—as expected, since the semilocal part E_{xc}^0 also contributes to the induced density—we find the same behavior as in Fig. 1: more down density is being pulled into the bond, strengthening the binding.

It is also revealing to partition the charge and magnetic moment of the system, as detailed in Table S2 in the Supplemental Material [68]. Partitioning schemes are not unique, but one can still gain qualitative information. Before adsorption, the CO_2 has no magnetic moment and all six Ni atoms in the unit cell are equivalent. However, once adsorption occurs, the up and down charge inside the CO_2 rearranges differently and gives rise to a small but observable magnetic moment. At the same time, the adsorption process leaves the total charge on the CO_2 molecule unchanged; i.e., there is no net charge transfer. During this adsorption process, the nearby Ni loses $0.03e$— our analysis shows that it loses mostly down density—and thus its magnetic moment increases, giving rise to a weak nonlocal correlation-induced magnetic interaction.

Finally, in terms of absolute numbers, spin effects in the Fe-MOF74 $+ CO_2$ and Co-MOF74 $+ CO_2$ systems seem to worsen agreement with experiment—but, at the same time, they actually resolve a more pressing issue. Experimentally, the CO_2 binding strength should follow the order Mn < Fe < Co < Ni. In calculations without spin (not considering the artificial case of Mn), the order is reversed. However, after including spin effects the correct order is restored.

In summary, we have developed a consistent spin-polarized version of the nonlocal exchange-correlation functional vdW-DF, which we find to now become an all-purpose functional. We then apply this framework to study small-molecule adsorption in MOF74 with magnetic open metal sites and find that including nonlocal spin effects can significantly influence the binding of the adsorbates. In the case of Ni-MOF-74 $+ CO_2$ we find a counterintuitive increase in binding due to nonlocal spin effects, which we explain by a coincidental interaction of the Ni d and O p states. The additional degree of freedom from such unexpected magnetic interactions can be used to tailor the specificity of MOFs in novel gas storage, sequestration, and sensing applications.

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