

TDDFT+ U : A critical assessment of the Hubbard U correction to exchange-correlation kernels and potentials

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We develop a generalization of the Kohn-Sham density-functional theory (KS-DFT)+Hubbard U (DFT+ U) method to the excited-state regime. This has the form of Hubbard U corrected linear-response time-dependent DFT, or “TDDFT+ U .” Combined with calculated linear-response Hubbard U parameters, it may provide a computationally light, first-principles method for the simulation of tightly bound excitons on transition-metal ions. Our presented implementation combines linear-scaling DFT+ U and linear-scaling TDDFT, but the approach is broadly applicable. In detailed benchmark tests on two Ni-centered diamagnetic coordination complexes with variable U values, it is shown that the Hubbard U correction to an approximate adiabatic semilocal exchange-correlation interaction kernel lowers the excitation energies of transitions exclusively within the targeted localized subspace by increasing the exciton binding of the corresponding electron-hole pairs. This partially counteracts the Hubbard U correction to the exchange-correlation potential in KS-DFT, which increases excitation energies into, out of, and within the targeted localized subspace by modifying the underlying KS-DFT eigenspectrum. This compensating effect is most pronounced for optically dark transitions between localized orbitals of the same angular momentum, for which experimental observation may be challenging, and theoretical approaches are at their most necessary. Interestingly, we find that first-principles TDDFT+ U seems to offer a remarkably good agreement with experiment for a perfectly closed-shell complex on which approximate TDDFT underperforms, but only when TDDFT+ U is applied to the DFT eigenspectrum and not to the DFT+ U one. In tests on an open-shell, noncentrosymmetric, high-spin cobalt coordination complex, we find that first-principles TDDFT+ U again compensates for the DFT+ U blueshift in $3d \rightarrow 3d$ transitions, but that using the DFT eigenspectrum is not viable due to the emergence of a singlet instability. Overall, our results point to shortcomings in the contemporary DFT+ U corrective potential, either in its functional form, or when applied to transition-metal orbitals but not to ligand ones, or both.

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I. INTRODUCTION

Density-functional theory (DFT) [1,2] provides a computationally tractable means by which to investigate the quantum mechanically derived properties of molecules and materials. TDDFT [3] is its elegant extension to the dynamical, excited-state regime. TDDFT is now widely used to investigate the excitation spectra of extended solids and molecules alike [4–6], due to its relatively low computational cost relative to wave-function and Green’s function-based approaches. While DFT and TDDFT are both exact in principle, their accuracies in practice are limited by the approximations currently available for the exchange-correlation (xc) contribution to the total-energy functional E_{xc} and its derived interaction kernel (by second functional derivatives), f_{xc} . Common xc functionals include local functionals such as the local density approximation [2], semilocal functionals such as generalized gradient approximations [7], and semiempirical functionals such as hybrids [8–10]. In practice, an adiabatic, i.e., time-averaged interaction approximation is made to construct the xc kernels of contemporary applied TDDFT. The latter is often also restricted, for expediency, to the linear-response regime appropriate only to low-energy, low-oscillator-strength excitations.

A. Self-interaction error in approximate DFT and its correction by Hubbard U based methods

Perhaps the most transparent systematic error exhibited by approximate functionals is the single-particle self-interaction error (SIE) [11], i.e., the tendency of electrons to effectively self-repel, and it has been demonstrated clearly in single-electron systems such as the molecule H_2^+ [12–15]. This error becomes more complicated in the many-body case, and hence, by necessity, there has emerged the more general concept of many-body self-interaction error [16], also known as delocalization error [17–22], which has been developed to understand the collective spurious self-interaction of approximated electron densities. In a system with a continuously variable occupation number, many-body SIE may be defined as the deviation from piecewise linearity of the approximate DFT total energy with respect to the total electron count [23].

The SIE is most problematic for systems comprising spatially localized, partially filled frontier orbitals including those of $1s$ and $2p$ but more canonically $3d$ and $4f$ character, where the qualitative failure of local and semilocal functionals has been thoroughly analyzed [24–27]. First-row transition metal systems thus can often benefit from corrective measures that augment conventional closed-form density functionals. An

approach that is very widely used at present is the computationally expedient $DFT+U$, which has been successfully applied to both extended solids [24,26,28–33] and molecular systems [34–39] alike.

$DFT+U$ attains the status of a first-principles method through the direct calculation of the requisite Hubbard U parameters, and for which a number of methods have been proposed [27,32,39–42]. We refer the reader to Ref. [43] for a recent detailed analysis of Hubbard U and Hund's J (the analogous quantity for quantifying erroneous energy-magnetization curvature in approximate DFT) calculation in the case of open-shell systems. $DFT+U$ is compatible with linear-scaling methods [44,45] intended for spatially complex systems, as well as with high-throughput materials discovery approaches [46,47]. Beginning with Ref. [40], and continued in Refs. [33,36,37,48], the concept of $DFT+U$ as a corrective method for SIE has been extensively developed, with the Hubbard U parameters playing the role of localized error quantifiers of SIE for the approximate functional applied to the specific system at hand [27]. We invoke this interpretation in what follows.

B. Self-interaction error in the excited-state regime

For the integer-occupancy systems routinely simulated, the generalized Koopman's condition [49] gives a unified, practicable expression for the SIE-free condition, the noncompliance with which is, in most cases, responsible for the underestimated insulating gaps [22,50] emblematic of practical DFT. When this cannot obviously be enforced, however, such as in neutral excited states, it will be helpful to decompose SIE into two contributions. The first is an overestimation of the net self-repulsion of the electron density due to the spurious self-interaction of individual electron densities, particularly so for localized atomic orbitals, which gives rise to a positive energy-occupancy curvature, over-delocalized of densities, and inaccurate ground-state total energies. The second is the lack of any distinction between the density due to electrons already existing in a system and that due to any newly removed or added electrons, which results in the spurious absence of derivative discontinuities in the energy-occupancy curve and, consequently, the shallowing of electron removal and addition levels and the underestimation of insulating gaps. Adiabatic linear-response TDDFT inherits both components of SIE from the underlying approximate DFT functional. In this work, we will focus on the former component while treating the latter only at the level available within first-principles $DFT+U$. Technically, we use $DFT+U$ in its simplified rotationally invariant formalism (which does not introduce a derivative discontinuity but emulates the effects of one in the Kohn-Sham [2] eigenspectrum), with first-principles linear-response Hubbard U and Hund's J parameters.

The effect of SIE on electron dynamics and neutral electronic excitations, such as those routinely studied using TDDFT, has slowly attracted increasing investigation in recent years [51–54]. It is a matter of central importance, for example, in the first-principles simulation of out-of-equilibrium nanoscale functionalities such as dynamical Coulomb blockade [55,56], and in the first-principles spectroscopy of systems comprising transition-metal ions [57–62]. In the realm of nonatomistic calculations, the TDDFT solution of

Hubbard-type models has also attracted attention [63–66], and TDDFT has also been combined with dynamical mean-field theory [67,68].

C. Motivation: Hubbard U correction in the excited-state regime of TDDFT

Somewhat surprisingly, perhaps, given its relatively moderate computational cost and conceptual simplicity, the error correction of approximate TDDFT by means of $DFT+U$, in the guise of adiabatic TDDFT+ U , has received relatively little attention to date. TDDFT+ U is readily compatible with linear-scaling DFT, as demonstrated in the present work though the combination of linear-scaling $DFT+U$ [44,45] and linear-scaling TDDFT [69–71], as well as with high-throughput materials screening techniques, where $DFT+U$ is commonplace [46]. Within its range of applicability, TDDFT+ U could potentially offer substantial efficiency advantages over more involved methods for calculating neutral excitations in complex transition-metal molecules and solids. These include hybrid TDDFT [72,73] and Green's-function-based methods such as GW +Bethe-Salpeter [74]. Recently, the optimally tuned, range-separated hybrid functionals [75,76] within TDDFT have met with promising success in the prediction of optical excitations, particularly in the lowest excitations in organic molecules and third-row transition-metal coordination complexes [77–79]. This latter approach has not been applied to any first-row transition-metal molecules yet, to our knowledge.

The role of $DFT+U$ in calculated excitation energies, particularly the explicit contribution from the Hubbard term, has been explored in Ref. [80]. The first reported TDDFT+ U implementation was that of Ref. [81], combining real-time propagation and a plane-wave basis, followed by Ref. [82], which detailed the results of a linear-response implementation applied to bulk NiO. In that system, TDDFT+ U was shown to be capable of reproducing the experimentally observed, tightly bound Frenkel excitons, but not their multiplet structure. These are relatively exotic spectroscopic features that neither the adiabatic LDA, nor the random phase approximation built from $LDA+U$, succeeded in recovering to any extent. Recently, in Ref. [83], a real-time plane-wave TDDFT+ U implementation has been coupled with Ehrenfest molecular dynamics to simulate both long- and short-ranged dynamical charge transfer between alkali atom impurities and conjugated carbon systems. This work revealed the tendency for an increasing Hubbard U to promote the availability of multiple low-energy states in such systems, as well as to increase in energy and broaden the impurity-bath charge-transfer resonances.

To date, however, information has been lacking on how the Hubbard U correction affects the typical products of practical TDDFT calculations in simple transition-metal systems, namely the low-energy excitation spectra and dipole-dipole absorption spectra, for better or worse with respect to experiment. Indeed, the precise effects of TDDFT+ U have yet to be systematically studied, and its resulting range of applicability has yet to be mapped out in any sense. It is this knowledge gap that we seek to begin to fill with the present exploratory study.

D. Outline of the paper: Systematic decomposition of the effects of the Hubbard U correction in Kohn-Sham DFT and linear-response TDDFT

We seek to systematically investigate the role of DFT+ U as it *separately* alters the Kohn-Sham eigenspectrum underlying a linear-response TDDFT calculation, and the TDDFT interaction kernel itself. For this, following its detailed introduction via an illustrative four-level toy model in Sec. II, we uncover the effects of full TDDFT+ U , in Sec. III, on two representative diamagnetic nickel complexes (one perfectly closed-shell, one less so), which were chosen for study due to their relatively simple coordination chemistry. Since their Ni $3d$ subshells are close to being fully filled, nominally, the dominant errors in the description of these molecules using an approximate semilocal xc functional [in this work always Perdew-Burke-Ernzerhof (PBE) [7]] and xc kernel (adiabatic PBE) may be ascribed primarily to SIE (electron delocalization) rather than static (multireference) correlation error [11,50]. For these systems, in Sec. IV, we show that first-principles Hubbard U correction at the TDDFT level alone, leaving the underlying Kohn-Sham eigenspectrum at its DFT level, offers a far better agreement with available experimental and quantum-chemical data when compared to either uncorrected DFT & TDDFT or consistent DFT+ U & TDDFT+ U . Performing Hubbard U correction at the DFT level alone meanwhile, leaving the TDDFT kernel uncorrected, leads to very unreasonable results indeed. We will discuss some implications and possible solutions to this intriguing asymmetry in Sec. VI.

We will turn first, however, in Sec. V, to the technically challenging case of an open-shell system, a noncentrosymmetric, high-spin cobalt coordination complex. Here, we will again find that a first-principles DFT+ U correction applied only to the Kohn-Sham eigenspectrum drastically degrades the agreement between the singlet excitation and the dipole-dipole absorption spectra and, respectively, high-level quantum-chemical and experimental data. The agreement is recovered to some degree when TDDFT+ U is also used, but a number of important spectral features remain poorly described. In this case, we will show that the application of first-principles TDDFT+ U upon the DFT Kohn-Sham eigenspectrum is not a viable workaround, as the implied inconsistency leads to the emergence of a singlet instability.

II. HUBBARD CORRECTION OF THE EXCHANGE-CORRELATION KERNEL: THEORY AND NUMERICAL ILLUSTRATION

Let us now introduce the anatomy of the Hubbard U correction to approximate TDDFT. Concerning ourselves only with low-energy single-particle excitations, we will restrict ourselves to the linear-response regime.

Here, the spin-unpolarized TDDFT problem may be expressed in the occupied-unoccupied Kohn-Sham eigenvector product space via Casida's equation [84,85], which is an eigenequation for the vertical excitation frequencies ω , given in its canonical notation by

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{A}^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ -\mathbf{Y} \end{pmatrix}. \quad (1)$$

The Hamiltonian matrix elements $A_{cv,c'v'} = \delta_{vv'}\delta_{cc'}\omega_{c'v'} + K_{cv,c'v'}$ and $B_{cv,c'v'} = K_{cv,v'c'}$ correspond to excitation-excitation pairs and excitation-relaxation pairs, respectively. The neglect of coupling between these processes, that is, the approximation $\mathbf{B} = \mathbf{0}$, is known as the Tamm-Dancoff approximation (TDA). The ground-state Kohn-Sham eigenvalues ϵ_v are those of occupied valence states, while the ϵ_c are those of unoccupied conduction states. The coupling matrix \mathbf{K} incorporates all interactions between particle-hole pairs, which is to say all effects beyond the many-body random-phase approximation [Fermi's golden rule (FGR)]. It is given, within the valence-conduction (cv) product representation of the interaction kernel \hat{f} , by

$$K_{cv,c'v'} = \iiint d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \psi_c^*(\mathbf{r})\psi_{v'}(\mathbf{r}') \times f(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''')\psi_{c'}(\mathbf{r}'')\psi_{v'}^*(\mathbf{r}'''), \quad (2)$$

where the ψ are Kohn-Sham eigenvectors. The kernel ordinarily comprises Hartree and xc terms only, denoted by \hat{f}_H and \hat{f}_{xc} , but if a DFT+ U derived correction term \hat{f}_U is added, the resulting TDDFT+ U interaction kernel is given by $\hat{f} = \hat{f}_U + 2(\hat{f}_H + \hat{f}_{xc})$. The underlying Kohn-Sham eigensystem is also changed, typically. The factor of 2 here is conventional, and it represents the sum of identical (in the unpolarized case) like- and unlike-spin Hartree and xc interactions acting on a given excitation. This factor of 2 does not, however, pre-multiply \hat{f}_U , since DFT+ U ordinarily acts explicitly only on like-spin Kohn-Sham states. The rotationally invariant DFT+ U energy functional [26,28–31] used in this work falls into this category, being given, for a SIE-affected subspace, by

$$E_U = \frac{U_{\text{eff}}}{2} \sum_{\sigma} \sum_m \left(n_{mm}^{\sigma} - \sum_{m'} n_{mm'}^{\sigma} n_{m'm}^{\sigma} \right), \quad (3)$$

where $U_{\text{eff}} = U - J$ is the effective like-spin correction parameter expressed in terms of the Hubbard U and the Hund's J parameter. The index σ is for spin, and the subspace occupancy matrix $n_{mm'}^{\sigma} = \sum_v \langle \varphi_m | \psi_v^{\sigma} \rangle \langle \psi_v^{\sigma} | \varphi_{m'} \rangle$ is typically defined in terms of localized orbitals (in our calculations, orthonormal atomic nickel or cobalt $3d$ orbitals solved in a norm-conserving pseudopotential), φ_m . The Hubbard U kernel is the second functional derivative [3] of the DFT+ U energy E_U with respect to the density matrix, and we find, denoting the density-matrix for spin σ by $\rho^{\sigma}(\mathbf{r}, \mathbf{r}')$, that

$$\begin{aligned} f_U^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= \frac{\delta^2 E_U[\rho^{\sigma}, \rho^{\sigma'}]}{\delta \rho^{\sigma}(\mathbf{r}'', \mathbf{r}''') \delta \rho^{\sigma'}(\mathbf{r}, \mathbf{r}')} \\ &= -U_{\text{eff}} \sum_{mm'} \delta^{\sigma\sigma'} \varphi_m(\mathbf{r}) \varphi_{m'}^*(\mathbf{r}') \varphi_m^*(\mathbf{r}'') \varphi_{m'}(\mathbf{r}'''). \end{aligned} \quad (4)$$

The resulting Hubbard U contribution to \mathbf{K} may be written, using implicit summation of paired indices, as

$$\begin{aligned} K_{cv,c'v'}^U &= -U_{\text{eff}} \langle \psi_c | \varphi_m \rangle \langle \varphi_{m'} | \psi_v \rangle \langle \psi_{c'} | \varphi_m \rangle \langle \varphi_{m'} | \psi_{v'} \rangle^* \\ &= -U_{\text{eff}} \langle \psi_c | \varphi_m \rangle \langle \varphi_m | \psi_{c'} \rangle \\ &\quad \times \langle \psi_{v'} | \varphi_{m'} \rangle \langle \varphi_{m'} | \psi_v \rangle, \end{aligned} \quad (5)$$

whereafter we will use U rather U_{eff} for simplicity, except where discussing our actual calculated U_{eff} . The resulting “direct” term, in what can be seen as an effective exciton self-interaction correction, is given by

$$K_{cv,cv}^U = -U \sum_{mm'} |\langle \psi_c | \varphi_m \rangle|^2 |\langle \psi_v | \varphi_{m'} \rangle|^2. \quad (6)$$

The form of \mathbf{K}^U hints at the behavior expected of the TDDFT+ U excitation spectrum as U is varied. For $U > 0$ eV, the interaction correction due to one (cv) pair and acting upon another is a sum over (typically) attractive direct Hartree and exchange terms. Relative to the situation that holds in hybrid-exchange TDDFT, however, the exchange terms are expected to be more significant relative to direct Hartree ones, since in TDDFT+ U the same constant U premultiplies both term types. It is instructive to examine the special case in which the projecting orbitals φ_m are identical to a subset of the underlying Kohn-Sham states ψ . There, the Hubbard U contributions to \mathbf{B} and \mathbf{A} reduce considerably to

$$\begin{aligned} A_{cv,c'v'}^U &= -U \delta_{cm} \delta_{m'c'} \delta_{v'm'} \delta_{m'v} = -U \delta_{cc'} \delta_{vv'}, \\ B_{cv,c'v'}^U &= -U \delta_{cm} \delta_{m'v'} \delta_{c'm'} \delta_{m'v} = 0, \end{aligned} \quad (7)$$

leaving a fully diagonal contribution to the Casida Hamiltonian. If these Kohn-Sham states are also well separated from all others energetically, the effect of the Hubbard U on the underlying eigenstate differences $\epsilon_c - \epsilon_v$ will simply be an increase by U , whereupon the effects of DFT+ U and TDDFT+ U *fully cancel* for excitations coupling states within the target subspace.

This picture is complicated by Kohn-Sham state hybridization, self-consistency, and the spillage of the localized orbitals, in practice. Nonetheless, the TDDFT+ U correction may be expected to increase the mixing of transitions between states that overlap strongly with the selected subspace, and to increase their exciton binding energy by compensating for the underlying DFT+ U eigenvalue correction. However, the matrix elements of \mathbf{K}^U are quadratic in overlap integrals of the form $\langle \psi_c | \varphi \rangle \langle \varphi | \psi_c \rangle$, whereas the underlying Hubbard U correction to the Kohn-Sham potential comprises terms that are only linear in such integrals. Thus, we cannot generally expect the cancellation of the U correction to the ground- and excited-state systems to be precise in practical calculations.

A. Illustration of the effect of U correction in TDDFT using a four-level toy model

For further insight, the effects of TDDFT+ U in conjunction with DFT+ U can be illustrated by means of a toy model in conjunction with the TDA and full Casida equation. Let us consider four independent-particle (KS-like) states, of which two occupied and two unoccupied states are labeled with $\{v, v'\}$ and $\{c, c'\}$, respectively, with some arbitrary eigenenergies as illustrated in Fig. 1. The pair $\{c, v\}$ of states shown by a dashed red line are targeted with a correction inspired by DFT+ U and TDDFT+ U .

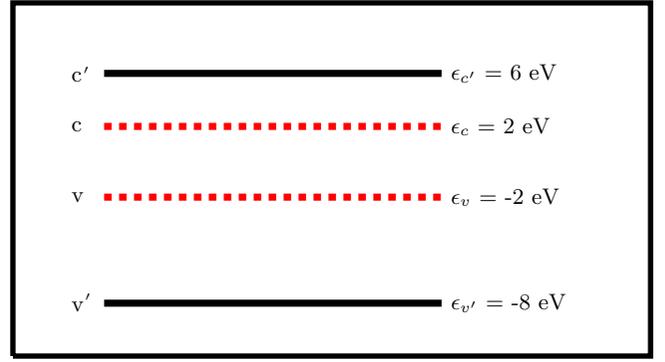


FIG. 1. A four-level toy model for independent-particle (Kohn-Sham orbital emulating) states of arbitrarily assigned energies, comprising two levels affected by U corrections and illustrated with dashed red lines and two bystander levels illustrated with black lines.

The block matrices \mathbf{A} and \mathbf{B} in the Casida equation become 4×4 matrices with elements given by

$$A_{ji,j'i'} = \left[(\epsilon_{j'} - \epsilon_{i'}) + \frac{U_{\text{DFT}}}{2} (\delta_{j'c} + \delta_{i'v}) - U_{\text{TDDFT}} \delta_{j'i',cv} \right] \delta_{i'i} \delta_{j'j} + K_{ji,j'i'}^{\text{Hxc}}, \quad (8)$$

$$B_{ji,j'i'} = K_{ji,j'i'}^{\text{Hxc}}, \quad (9)$$

where j and j' run over $\{c, c'\}$, while i and i' run over $\{v, v'\}$. The Hubbard parameter U_{DFT} imitates the effect of DFT+ U by pushing the targeted states away from the Fermi level via the term $U_{\text{DFT}}(\delta_{j'c} + \delta_{i'v})/2$, whereas the Hubbard parameter U_{TDDFT} includes the effect of TDDFT+ U via the term $-U_{\text{TDDFT}} \delta_{j'i',cv}$. By making these two Hubbard parameters U_{DFT} and U_{TDDFT} independent, the individual effects of the Hubbard corrections at the DFT and TDDFT levels can be observed by setting one of them to zero at a time. The Hartree+xc coupling matrix elements are assigned for illustration here to the arbitrary values

$$\begin{aligned} K_{ji,j'i'}^{\text{Hxc}} &= \begin{cases} 4.0 \text{ eV} & \text{for } \delta_{ji,j'i'} \\ 0.8 \text{ eV} & \text{otherwise,} \end{cases} \\ K_{ji,j'i'}^{\text{Hxc}} &= \begin{cases} 4.0 \text{ eV} & \text{for } \delta_{ji,j'i'} \\ 0.8 \text{ eV} & \text{otherwise,} \end{cases} \end{aligned} \quad (10)$$

and the symmetric choice made here is a deliberate attempt to simplify the contributions due to f_{Hxc} .

The Casida equation, both in its full form and within the TDA, was solved using an eigenvalue solver over a range of U_{DFT} and U_{TDDFT} values. Additionally, FGR excitations energies are included and calculated as

$$\omega_{ji}^{\text{FGR}}(U_{\text{DFT}}) = (\epsilon_j - \epsilon_i) + \frac{U_{\text{DFT}}}{2} (\delta_{jc} + \delta_{iv}). \quad (11)$$

In Fig. 2, the principal effects of a positive U_{DFT} (simulating DFT+ U) and U_{TDDFT} (simulating TDDFT+ U) in our toy model are demonstrated via the amplitudes of normalized electronic excitation spectra (EES) calculated using Eq. (13). A Lorentzian lifetime broadening of $\Gamma = 0.1$ eV was used here, together with a high-resolution grid of Hubbard U

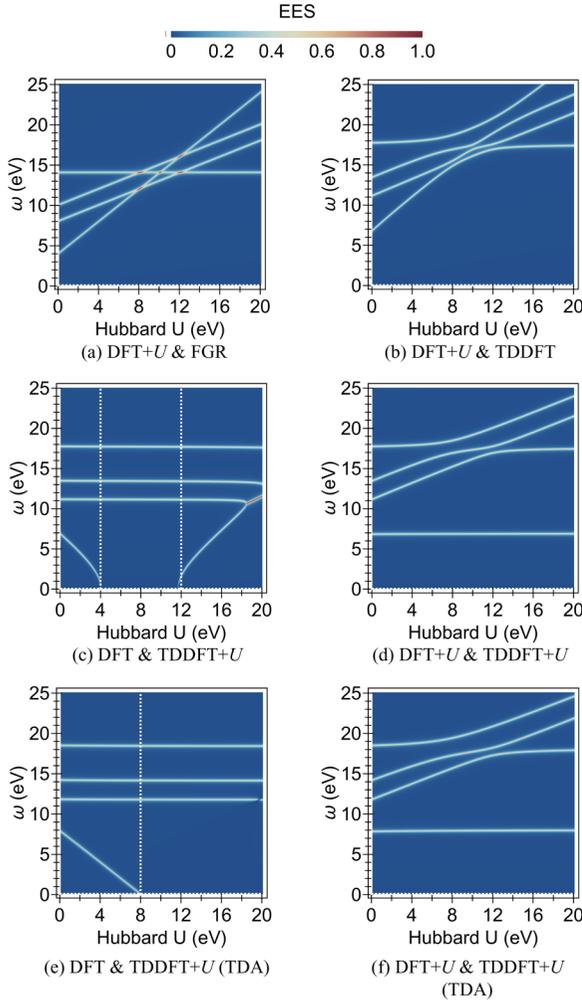


FIG. 2. Electronic excitation spectra (EES) calculated from our illustrative four-level toy model, using Eq. (13) with $\Gamma = 0.1$ eV. Subfigure captions indicate the analogous DFT-based approximation, e.g., the + U in “DFT+ U & FGR” indicates that the occupied (unoccupied) localized level is lowered (raised) by $U_{\text{DFT}}/2$ (with $U_{\text{TDDFT}} = 0$ eV), while “FGR” indicates that the transitions are treated as independent. On the other hand, “TDDFT” denotes that a repulsive kernel given by Eq. (10) couples transitions, while “TDDFT+ U ” indicates that said kernel is U -corrected by Eq. (8) with the Hubbard U axis denoting U_{TDDFT} . For “DFT+ U & TDDFT+ U ,” $U_{\text{DFT}} = U_{\text{TDDFT}}$. TDA is the Tamm-Dancoff approximation.

parameters taken in 0.05 eV steps. Starting from the energy levels shown in Fig. 1, a positive value of $U = U_{\text{DFT}}$ pushes the targeted (red dashed line in Fig. 1) states (v, c) away from the Fermi level, each by $U/2$, while the bystander states remain intact. Consequently, in Fig. 2(a), the excitation from v to c ($v \rightarrow c$) increases simply by U , while the energies of $v' \rightarrow c$ and $v \rightarrow c'$ increase by $U/2$, emulating the effects of DFT+ U . The remaining excitation $v' \rightarrow c'$ is not affected due to a lack of interaction between exciton pairs within FGR.

Comparing next Figs. 2(b), 2(c), and 2(d) against the FGR results of Fig. 2(a), each evaluated at $U = 0$ eV, a global shift by TDDFT of ~ 3 –4 eV on the excitation energies can be seen, as well as the avoided crossing of excitation energies for $U > 0$ eV. This is due to the interactions between exciton

pairs, emulating TDDFT, that are introduced by the coupling matrix $K_{ji,j'i'}^{\text{Hxc}}$ in Eq. (10). The global nature of the shift is due to the invariance of the coupling matrix with respect to the swapping of orbital indices. In Figs. 2(c) and 2(e), the U_{TDDFT} term (emulating TDDFT+ U) exclusively affects the excitation $v \rightarrow c$ by pushing it down (linearly in the TDA case) from ≈ 8 eV for increasing $U = U_{\text{TDDFT}}$ values. For $U = 4$ eV ($U = 8$ eV for TDA), the excitation $v \rightarrow c$ becomes purely imaginary (negative in the TDA case), meaning that the model becomes unphysical. In Fig. 2(d), the combined emulated effects of DFT+ U and TDDFT+ U , when $U_{\text{DFT}} = U = U_{\text{TDDFT}}$, are seen in the form of a total cancellation of the effect of DFT+ U on the excitation $v \rightarrow c$ by TDDFT+ U . The remaining three excitations are affected by DFT+ U as before, while the effect of TDDFT+ U [comparing Figs. 2(b) and 2(d)] is relatively minor and mostly due to avoided crossing.

Comparing Fig. 2(d) with its TDA counterpart Fig. 2(f), the excitations within this model show a similar qualitative behavior irrespective of whether the TDA is invoked. The TDA approximately shifts the excitations up in energy by ~ 1 eV throughout the frequency range.

B. Implementation of the TDDFT+ U kernel within linear-scaling linear-response TDDFT

We have implemented the TDDFT+ U kernel of Eq. (4) in the ONETEP package [45,86,87]. This direct-minimization DFT code maintains a linear-scaling increase in computational expense with respect to system size, while maintaining an accuracy that is effectively equivalent to that of a plane-wave code. It does this by expanding the Kohn-Sham density matrix in terms of a minimal set of spatially truncated nonorthogonal generalized Wannier functions (NGWFs), which are variationally optimized *in situ* [88]. For calculations involving excited states, the code is capable of variationally optimizing a set of Wannier functions for the unoccupied conduction bands in a postprocessing step that follows conventional total-energy minimization [89]. With this, and using the resulting joint basis of optimized valence- and conduction-band Wannier functions, we used the linear-scaling beyond-Tamm-Dancoff linear-response TDDFT functionality available in ONETEP [69–71], which again uses iterative minimization, as the basis for our implementation. The central element in our combination of linear-scaling TDDFT and DFT+ U [45] is the *change* in DFT+ U potential associated with the first-order change in Kohn-Sham density matrix, $\rho^{(1)}(\mathbf{r}, \mathbf{r}'; \omega)$, at each excitation energy ω , which is given by the same expression for both singlet and triplet excitations alike, specifically

$$\hat{V}_U^{\sigma(1)}(\omega) = -U \sum_{mm'} |\varphi_m\rangle \langle \varphi_m | \rho^{\sigma(1)}(\omega) | \varphi_{m'}\rangle \langle \varphi_{m'}|. \quad (12)$$

From this equation, it is clear that the occupancy dependence of the DFT+ U potential survives in TDDFT+ U , insofar as, for $U > 0$ eV, a level within the target subspace that is depopulated under excitation (typically a valence level close to the gap) will be subject to a more repulsive DFT+ U potential, whereas a repopulated (e.g., conduction) level will be subject to a more attractive DFT+ U potential. TDDFT+ U thus tends to promote such excitations by increasing the

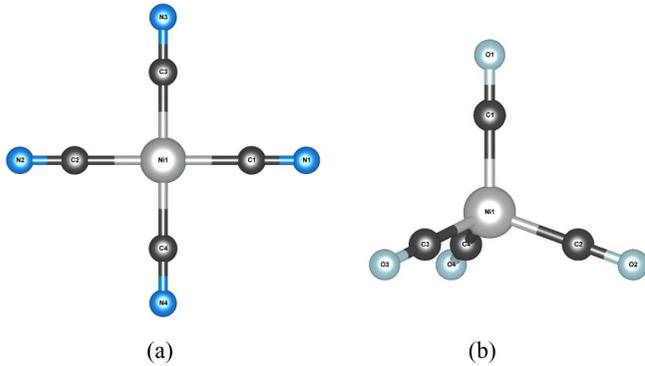


FIG. 3. The molecular structures of two representative Ni-centered closed-shell coordination complexes. Shown on the left is the planar tetracyanonickelate anion $\text{Ni}(\text{CN})_4^{2-}$, and shown on the right is the tetrahedral nickel tetracarbonyl $\text{Ni}(\text{CO})_4$.

exciton binding between the associated levels. We emphasize that the interaction in TDDFT+ U remains entirely adiabatic as it is presented here, since the kernel \hat{f}_U is constant in time, and so it addresses only the time average of the self-interaction error as it is measured in the ground state. As a result, it lacks the ability to produce dynamical step features in the potential that may result from occupancies passing through integer values, which are dynamical manifestations of the second aspect of self-interaction error previously discussed. However, TDDFT+ U does provide a convenient framework in which to explore nonadiabatic self-interaction correction kernels $\hat{f}_U(\omega)$ by means of an explicitly frequency-dependent Hubbard $U(\omega)$.

III. THE HUBBARD U DEPENDENCE OF NEUTRAL EXCITATION SPECTRA

Two small closed-shell Ni-centered coordination complexes, namely the planar tetracyanonickelate anion $\text{Ni}(\text{CN})_4^{2-}$ and tetrahedral nickel tetracarbonyl $\text{Ni}(\text{CO})_4$ shown in Fig. 3, were chosen for study. The Hubbard U dependence of molecular spectra, in terms of both its individual effects on DFT+ U and TDDFT+ U and on their combination, was investigated. These systems provide a useful playground in which to investigate the effects of DFT+ U and TDDFT+ U , since they minimize any complex contributions from magnetic ordering and large ligand-field splittings, as both systems are closed-shell and centrosymmetric with strong ligands. Furthermore, these systems have previously been studied experimentally [90–93] and using numerous first-principles methods [94–97]. This is not, however, to imply that these systems are ideal candidates for treatment using DFT+ U , let alone TDDFT+ U , since they are reasonably well described by conventional approximate DFT.

A. Convention for visualizing spectra

At this juncture, we must introduce our conventions for visualizing two essential molecular spectroscopies. Electronic excitation spectra (EES) are constructed here by including both optically allowed and forbidden excitations with the same unit oscillator strength. They are calculated using the

formula

$$\text{EES}(\omega) = \sum_{ij} \frac{\Gamma/2}{(\omega - \omega_{ji})^2 + (\Gamma/2)^2}, \quad (13)$$

where ω_{ji} denotes the energy of a transition from an occupied (i) to an unoccupied (j) molecular electronic state, and Γ is a Lorentzian broadening factor.

Electric dipole-dipole absorption spectra are commonly used to measure the optical response of molecules in the low-energy spectral range. The contributions of the individual excitations are weighted by oscillator strengths $f_{j \leftarrow i}$ related to the transition dipole moments. The formula relevant to optical absorption is

$$\text{ABS}(\omega) = \sum_{ij} f_{j \leftarrow i} \frac{\Gamma/2}{(\omega - \omega_{ji})^2 + (\Gamma/2)^2}, \quad (14)$$

and this type of spectrum is the one primarily used here for comparing with experimental observations.

EES and ABS were constructed using Eqs. (13) and (14) with a Lorentzian broadening $\Gamma = 0.1$ eV at integer values of the Hubbard U parameters, and interpolated to intermediate values in 0.01 eV steps. Our EES are scaled by setting the global maximum of EES data across DFT & TDDFT, DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U to unity. Similarly, our ABS are scaled by setting the global maximum of ABS data across all of these four combinations to unity. Such separate scaling factors enable us to compare relative intensities within various methods as well as to maintain the comparability between EES and ABS within same method. EES calculated within the FGR are scaled separately, using their own maxima.

B. The square-planar tetracyanonickelate anion: $\text{Ni}(\text{CN})_4^{2-}$

The square-planar $\text{Ni}(\text{CN})_4^{2-}$ is a low-spin coordination complex, with a Ni center of nominal charge 2+. $(\text{CN})^-$ is a strong-field π -acceptor ligand that leads to ligand-splitting of the $3d$ levels of Ni, following $d_{yz} \approx d_{xz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$, where $3d^8$ electrons occupy the first four levels and the remaining $3d_{x^2-y^2}$ forms a dsp^2 -hybrid with the ligands in the square-planar symmetry [98]. As a result, the low-lying excitations are expected to be predominantly of a mixed $3d \rightarrow 3d$ and metal-to-ligand $3d \rightarrow \pi^*$ character, as suggested by previous studies [96].

The energy alignment of $3d$ states is shown as a function of U in Fig. 4(a). For increasing U values, the occupied $3d$ states move to deeper energies. The states close to the highest occupied molecular orbital–lowest unoccupied molecular orbital gap (shown with red, dashed lines), which strongly contribute to low-lying excitations, combine with lower-energy states at about $U \gtrsim 7$ eV. Thus, low-lying excitations are pushed upwards, and ultimately they combine with higher-energy excitations of metal-to-ligand character, as seen in the EES calculated using FGR in Fig. 4(b).

Up to this point, the Hubbard U has been used only to modify the underlying KS-DFT states via DFT+ U . In Fig. 5, a more complete and consistent picture is provided by the EES for the first 50 singlet excitations calculated using various combinations of DFT+ U and TDDFT+ U . In Fig. 5(a), we

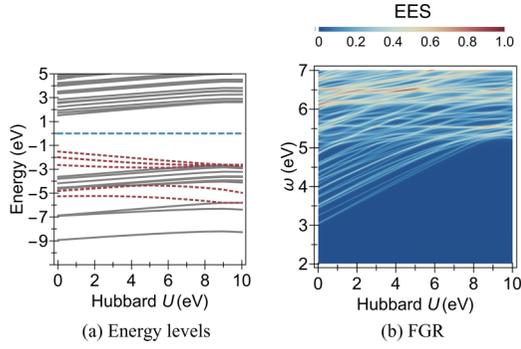


FIG. 4. The Kohn-Sham DFT+ U energy levels and singlet EES spectra of $\text{Ni}(\text{CN})_4^{2-}$ calculated using the FGR, as functions of the Hubbard U parameter. The Fermi level (dashed, blue line) is set to 0 eV. The states most strongly affected by DFT+ U are shown with dashed, red lines.

see that an increasing U value in DFT+ U reduces the $3d \rightarrow 3d$ character of the excitations, and combines them with excitations from deeper states, similarly to the FGR case. Beyond that, DFT+ U is effective globally insofar as it pushes other excitations to higher energies by means of modifying the metal-to-ligand energy as seen in Fig. 4(a).

On the contrary, in Fig. 5(b), we observe that TDDFT+ U affects only the excitations of $3d \rightarrow 3d$ character, while, as anticipated, the remaining excitations remain largely unaffected. Furthermore, the affected excitations become non-physical for $U \gtrsim 7$ eV in DFT & TDDFT+ U , similarly to what is observed in the four-level toy model. This situation, known as a singlet instability, arises by virtue of exciton

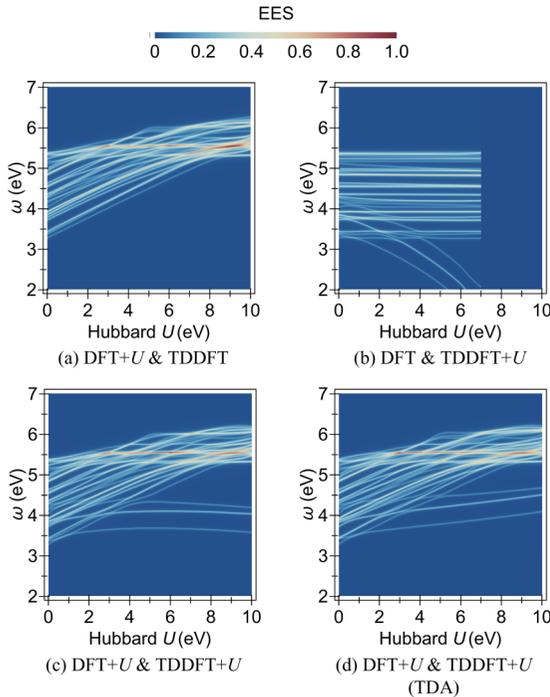


FIG. 5. The singlet EES of $\text{Ni}(\text{CN})_4^{2-}$, calculated using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U , as functions of the Hubbard U parameter.

overbinding, where for large values of U , the TDDFT+ U contributions to coupling matrix elements $K_{cv,cv}^U$ in Eq. (5) overcompensate for the sums of energy differences ω_{cv} and the Hartree+exchange-correlation contribution to coupling matrix elements, leading to unphysical complex eigenvalues. In Fig. 5(c) we find that, when DFT+ U and TDDFT+ U are combined consistently, TDDFT+ U primarily cancels the effects of DFT+ U on $3d \rightarrow 3d$ type excitations, which are in the ~ 3.5 – 4.5 eV range. This cancellation of DFT+ U by TDDFT+ U gives rise to an approximately quadratic net dependence on U within the full Casida equation, as opposed to a rather linear net behavior with U when the TDA is invoked. We can clearly observe this when comparing Fig. 5(c) and TDA in Fig. 5(d). This again reflects what was previewed in our four-level toy model.

Overall, on the one hand DFT+ U is very efficient at modifying the ABS as it pushes low-lying optical transitions to higher energies, as seen in Figs. 6(a), 6(c), and 6(d). On the other hand, TDDFT+ U does not have any significant effect at all on the ABS shown in Fig. 6(b), as TDDFT+ U acts solely on $3d \rightarrow 3d$ excitations, which are optically perfectly dark in $\text{Ni}(\text{CN})_4^{2-}$ here due to its idealized square-planar symmetry.

C. The tetrahedral nickel tetracarbonyl: $\text{Ni}(\text{CO})_4$

The tetrahedral $\text{Ni}(\text{CO})_4$ is another low-spin coordination with a neutral Ni center, but it is not perfectly isoelectronic with $\text{Ni}(\text{CN})_4^{2-}$ as it has an uncomplicated, full $3d$ subshell. The $(\text{CO})^-$ ion is a strong-field π -acceptor ligand, which splits the $3d$ states of Ni into $d_{z^2} \approx d_{x^2-y^2} < d_{xy} \approx d_{xz} \approx d_{yz}$ due to the tetrahedral symmetry present. The twofold- and threefold-degenerate $3d$ splitting can be clearly distinguished by the differing response to DFT+ U seen in Fig. 7(a). In this

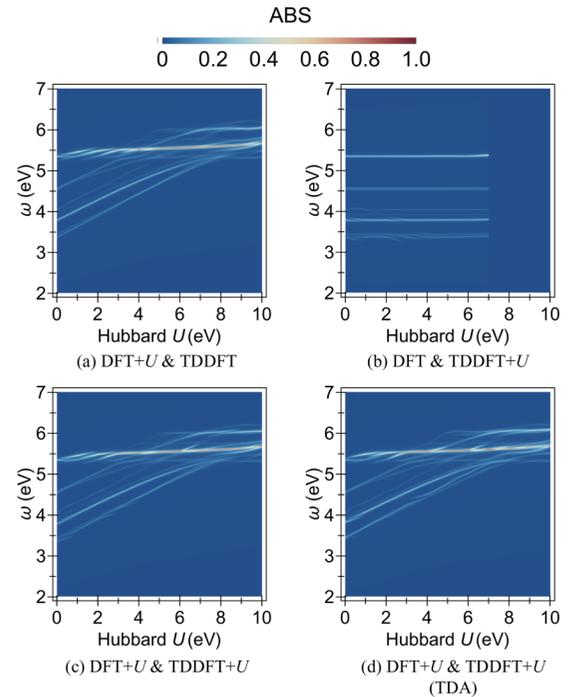


FIG. 6. The dipole-dipole absorption spectra of $\text{Ni}(\text{CN})_4^{2-}$, calculated using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U , as functions of the Hubbard U parameter.

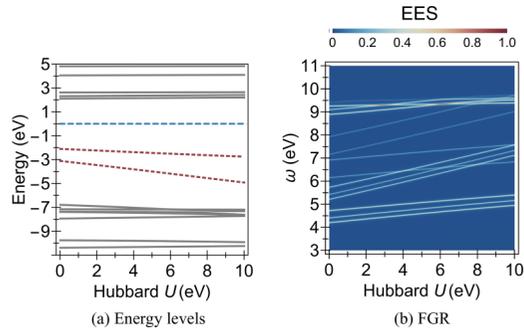


FIG. 7. The Kohn-Sham DFT+ U energy levels and singlet EES spectra of Ni(CO) $_4$ calculated using the FGR, as functions of the Hubbard U parameter. The Fermi level (dashed, blue line) is set to 0 eV. The states most strongly affected by DFT+ U are shown with dashed, red lines.

system, the low-lying singlet excitations are necessarily of a predominantly Ni $3d \rightarrow \pi^*$ character [93,99].

In Fig. 7(a), we observe that the twofold-degenerate $d_{z^2} \approx d_{x^2-y^2}$ states (red, dashed line) at -2 eV and the threefold-degenerate $d_{xy} \approx d_{xz} \approx d_{yz}$ states (red, dashed lines) at -3 eV for $U = 0$ eV are pushed deeper with increasing U values within DFT+ U . In Fig. 7(b), these immediate effects of DFT+ U on the low-lying $3d \rightarrow \pi^*$ excitations at ~ 4.0 – 5.5 eV for $U = 0$ eV are reflected in upshifts in the FGR singlet EES with increasing U values. Such shifts are larger for excitations from the d_{z^2} and $d_{x^2-y^2}$ states, as these are lowered more by DFT+ U .

A complete picture of the behavior of the first 50 excitations with DFT+ U and TDDFT+ U is presented in Fig. 8. The increasing U parameter in DFT+ U affects excitation energies

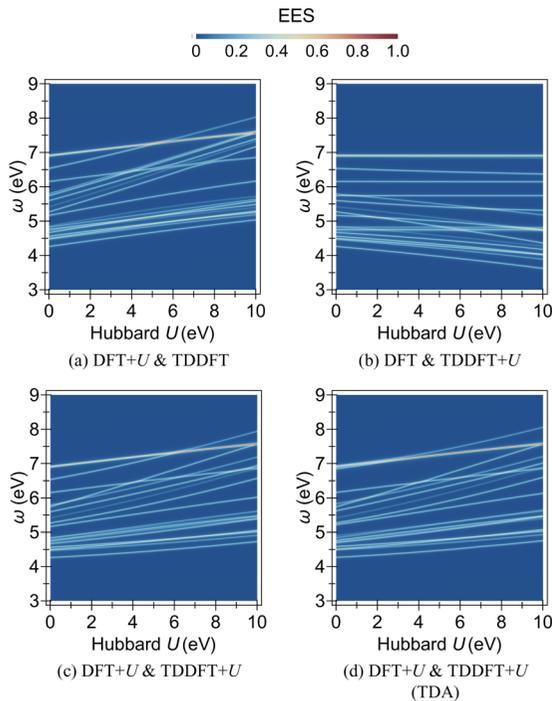


FIG. 8. The singlet EES of Ni(CO) $_4$ calculated using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U , as functions of the Hubbard U parameter.

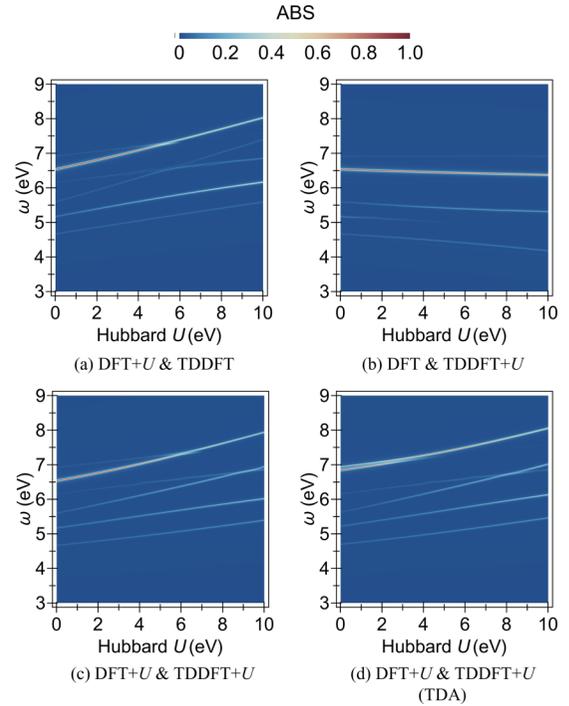


FIG. 9. The dipole-dipole absorption spectra of Ni(CO) $_4$ calculated using DFT+ U & TDDFT, DFT & TDDFT+ U , and DFT+ U & TDDFT+ U as functions of the Hubbard U parameter.

globally by pushing them to higher energies. In Fig. 8(a), particularly, the excitations from the lower-lying $3d$ levels ($d_{z^2}/d_{x^2-y^2} \rightarrow \pi^*$) at ~ 5 – 6 eV for $U = 0$ eV climb most strongly and cross over with the excitations from the deeper states at around $U \approx 4$ eV, as was previewed in Fig. 7(b). A similar trend is also present with DFT+ U as it is more effective on the excitations from the lower-energy $3d$ levels, as seen in Fig. 8(b), where some crossover occurs with the lower-energy group of excitations. The cancellation of DFT+ U effects by TDDFT+ U is more subtle in Ni(CO) $_4$ for the relevant excitations compared to the situation in Ni(CN) $_4^{2-}$, and this [shown in Fig. 8(c)] is as expected due to the weaker $3d \rightarrow 3d$ character of the transitions. While TDDFT+ U shifts the lowest group of excitations as well as splitting these excitations, it does not lead to the splitting-off of distinct tightly bound excitons as observed in Ni(CN) $_4^{2-}$. As the dominant optically allowed transitions are almost purely of $3d \rightarrow \pi^*$ character, DFT+ U naturally pushes bright excitations up in energy, as seen in Fig. 9(a), whereas the effect of TDDFT+ U on these excitations is quite subtle, which can be seen in Fig. 9(b). An important point to recall here is that, while DFT+ U is effective in proportion to the $3d$ character of the KS manifold, TDDFT+ U is proportional to the $3d$ character of product space of occupied $3d$ -unoccupied $3d$ subspaces.

IV. FIRST-PRINCIPLES SPECTRA OF TWO LOW-SPIN NICKEL-CENTERED COMPLEXES

The EES and ABS of our two closed-shell coordination complexes were generated using DFT+ U and TDDFT+ U with their respective first-principles Hubbard U_{eff} parameters,

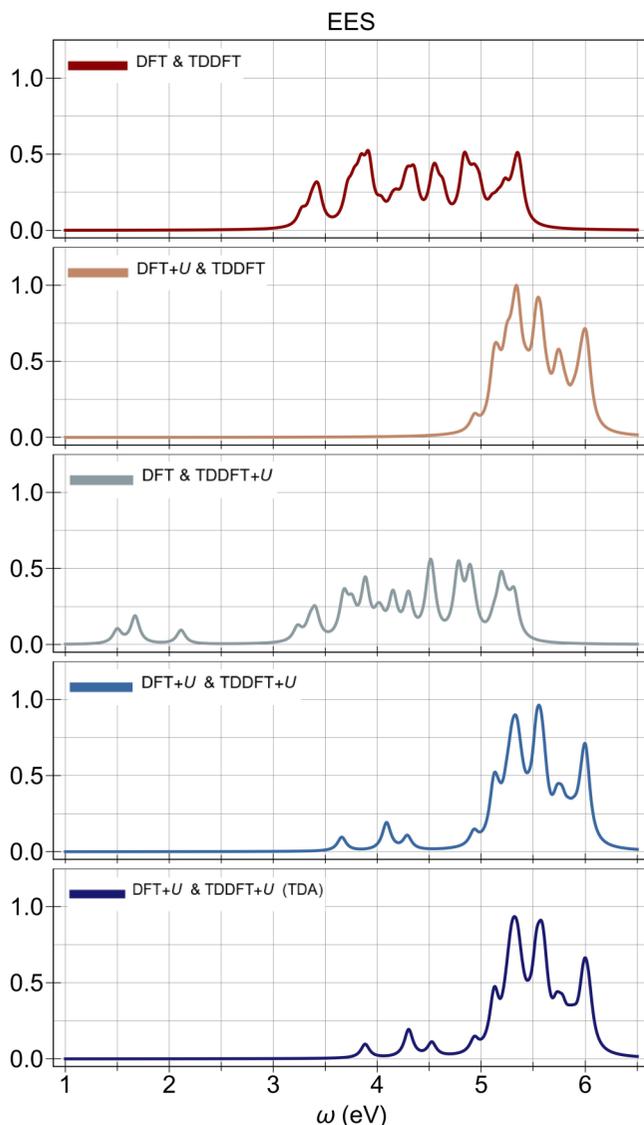


FIG. 10. The singlet EES of $\text{Ni}(\text{CN})_4^{2-}$ extracted from Fig. 5 by taking a cross section at the first-principles Hubbard $U_{\text{eff}} = 6.901$ eV, and shown with a Lorentzian broadening of 0.1 eV.

following the detailed procedure described in the Appendixes. In particular, these spectra were obtained by evaluating, or “slicing,” the interpolated data shown in the graphs presented in Secs. III B and III C, at the corresponding first-principles Hubbard U parameters summarized in Table V.

A. Excitation energies and spectra of $\text{Ni}(\text{CN})_4^{2-}$

The EES and ABS of $\text{Ni}(\text{CN})_4^{2-}$ are presented in Figs. 10 and 11 for the first-principles $U_{\text{eff}} = U - J = 6.901$ eV, alongside experimental excitation spectra extracted from Ref. [90]. In Fig. 11, the experimental excitation peak positions are shown with vertical gray lines, with heights indicating their relative absorbance with respect to that of the experimental maximum absorbance at 4.66 eV, which is set to unity.

Excitation energies are listed in Table I along with the experimental results [90] and TDDFT results [96], with optically bright excitations highlighted with a bold font. In particular,

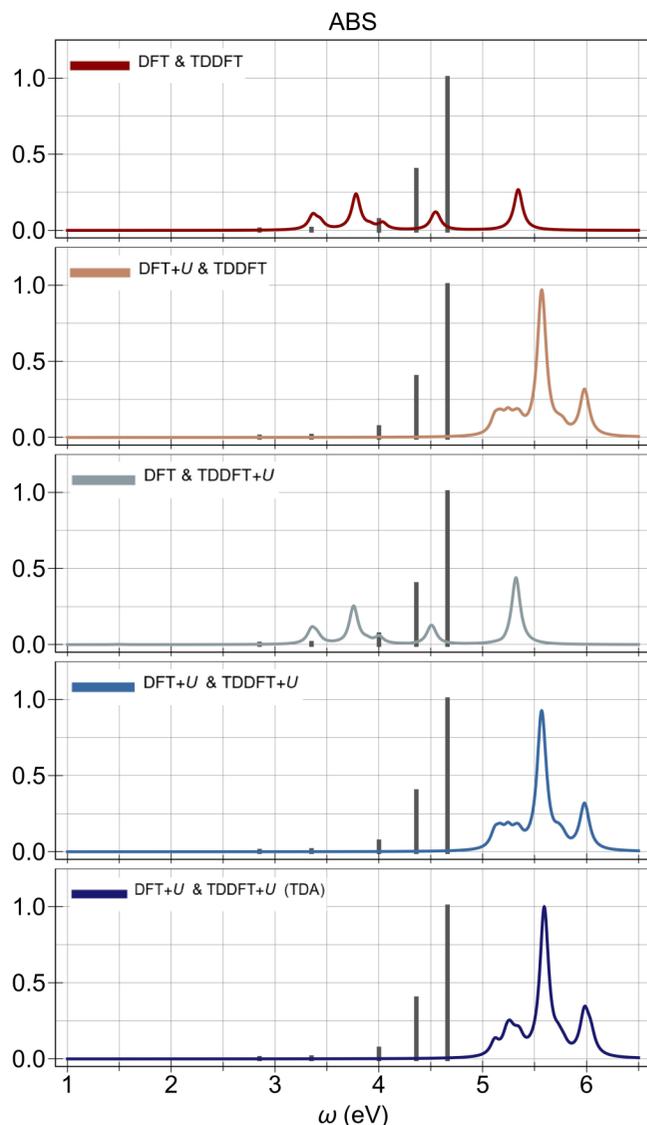


FIG. 11. The singlet dipole-dipole ABS of $\text{Ni}(\text{CN})_4^{2-}$ extracted from Fig. 6 by taking a cross section at the first-principles Hubbard $U_{\text{eff}} = 6.901$ eV, and shown with a Lorentzian broadening of 0.1 eV. The experimental absorption energies extracted from Ref. [90] are shown with vertical gray lines that are scaled with respect to the maximum absorbance of the highest energy peak at 4.66 eV.

our first-principles excitation energies were obtained from the peak positions of Fig. 10, with smaller peaks and shoulders removed, and the optically bright ones were assigned by matching to the peaks of Fig. 11.

The previous TDDFT calculations of Ref. [96] were performed using implicit solvation with a dielectric constant of 37.5, whereas ours were performed under vacuum conditions. Nonetheless, the former data provide a useful benchmark for testing the numerical validity of our TDDFT+ U code. As seen Fig. 10, DFT+ U is effective throughout the spectral range. It shifts excitation features to higher energies, as seen by comparing DFT+ U & TDDFT with DFT & TDDFT (PBE). TDDFT+ U , however, acts only in the low-energy range, and it gives rise to the emergence of new peaks surrounded by those already present in DFT & TDDFT. The

TABLE I. Energies (in eV) of the singlet excitations of $\text{Ni}(\text{CN})_4^{2-}$, as obtained without symmetry assignment from the peak positions of Fig. 10, with smaller peaks and shoulders removed. Coinciding peaks in Fig. 11 are assigned as optically bright excitations and highlighted with a bold font.

| Method | | | | | | |
|--------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| DFT & | 3.37 | 3.42 | 3.78 | 3.85 | 3.91 | 4.03 |
| TDDFT (PBE) | 4.34 | 4.55 | 4.84 | 4.92 | 5.23 | 5.34 |
| DFT+ U & | 4.94 | 5.17 | 5.24 | 5.33 | 5.57 | 5.74 |
| TDDFT | 5.98 | | | | | |
| DFT & | 1.50 | 1.67 | 2.11 | 3.24 | 3.36 | 3.68 |
| TDDFT+ U | 3.76 | 3.88 | 4.00 | 4.15 | 4.30 | |
| | 4.51 | 4.78 | 4.89 | 5.19 | 5.32 | |
| DFT+ U & | 3.66 | 4.09 | 4.29 | 4.93 | 5.17 | 5.24 |
| TDDFT+ U | 5.33 | 5.57 | 5.75 | 5.98 | | |
| DFT+ U & | 3.88 | 4.30 | 4.52 | 4.94 | 5.12 | 5.26 |
| TDDFT+ U (TDA) | 5.59 | 5.73 | 5.98 | | | |
| Expt. [90] | 2.85 | 3.35 | 4.00 | 4.36 | 4.66 | |
| TDDFT (PBE) [96] | 3.99 | 4.19 | 4.48 | 3.76 | 4.12 | 4.53 |
| TDDFT (LDA) [96] | 3.98 | 4.17 | 4.46 | 3.78 | 4.13 | 4.55 |
| TDDFT (B3LYP) [96] | 3.29 | 3.57 | 3.92 | 4.75 | 5.07 | 5.59 |

combined effects of DFT+ U and TDDFT+ U prove to be almost a simple combination of their respective individual effects, as seen in EES with DFT+ U & TDDFT+ U , where excitation energies are globally shifted and some additional peaks emerge.

In Fig. 11 (also represented in Table I), regardless of its flavor, TDDFT fails to capture the optically bright excitation at 2.85 eV observed in experiment, and this is consistent with previous TDDFT studies using the LDA and PBE functionals. Hybrid TDDFT using the B3LYP functional performs better than LDA or PBE in this regard, surely due to its better (more spatially long-ranged) description of exciton binding via its partial inclusion of the exact exchange interaction. In Fig. 11, we see that DFT+ U carries optically bright features to higher energies and dramatically changes the overall appearance of the spectrum. In fact, DFT+ U clearly worsens the agreement with experimental excitation energies. It pushes excitations within DFT+ U & TDDFT to higher energies such that the lowest optically bright excitation is carried to a position ~ 1.8 eV higher in energy compared to that of DFT & TDDFT. We find that TDDFT+ U has a relatively minor effect on the optically bright excitations when applied upon DFT (PBE), and no discernible effect when applied upon DFT+ U . Thus, TDDFT+ U does not mitigate the harmful effects of DFT+ U on optically bright excitations in this system. TDA and RPA predict spectra in close mutual agreement, with slightly higher energies emerging within TDA for both spectra.

B. Excitation energies and spectra of $\text{Ni}(\text{CO})_4$

The EES and ABS of $\text{Ni}(\text{CO})_4$ are presented in Figs. 12 and 13, respectively, for first-principles $U_{\text{eff}} = 9.849$ eV. Shown alongside, for comparison, are the corresponding spectra generated using the experimental excitation energies and oscillator strengths extracted from Ref. [93]. In this

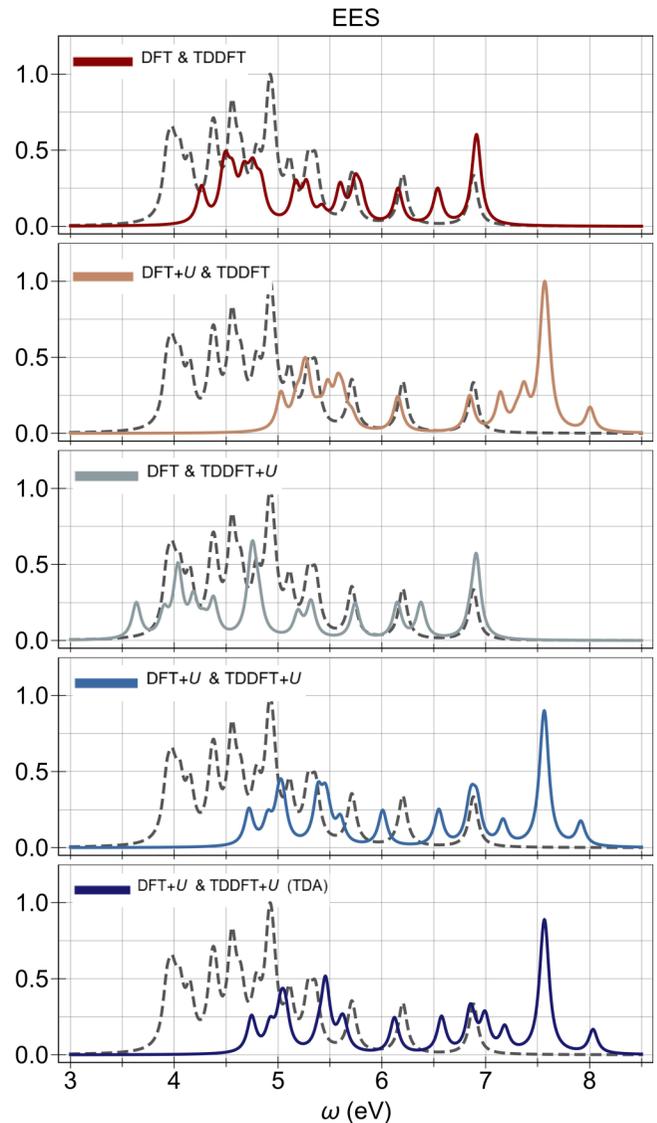


FIG. 12. The singlet EES of $\text{Ni}(\text{CO})_4$ extracted from Fig. 8 by taking a cross section at the first-principles Hubbard $U_{\text{eff}} = 9.849$ eV, and shown with a Lorentzian broadening of 0.1 eV. The EES (gray, dashed line), constructed from INDO/S quantum-chemical excitation energies extracted from Ref. [93], is shown with a Lorentzian broadening of 0.1 eV.

molecule, due to its less-than-full $3d$ manifold and hence increased $3d$ character of the valence-conduction transition space, we will see that TDDFT+ U is rather more effective than it is in the case of $\text{Ni}(\text{CN})_4^{2-}$. However, it is still not enough to compensate for the inaccuracy that the contemporary DFT+ U potential introduces, and, intriguingly, DFT & TDDFT+ U performs by far the best among the combinations tested.

In Fig. 13 (also in Table II), we observe that DFT & TDDFT overestimates the lowest optically bright excitation by ~ 1.1 eV compared to *in vacuo* INDO/S (the intermediate neglect of differential overlap model adapted for spectroscopy) quantum-chemical calculations. DFT+ U worsens this overestimation to ~ 1.4 eV, while arguably also worsening the line-shape agreement. TDDFT+ U applied upon this

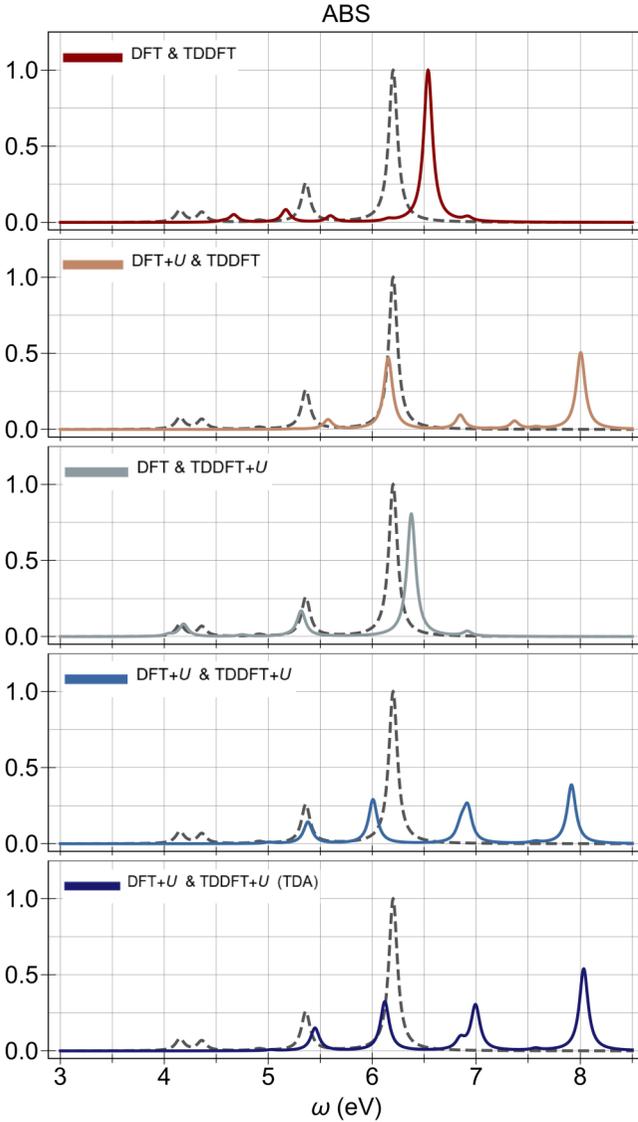


FIG. 13. The singlet dipole-dipole ABS of $\text{Ni}(\text{CO})_4$ extracted from Fig. 9 by taking a cross section at the first-principles Hubbard $U_{\text{eff}} = 9.849$ eV, and shown with a Lorentzian broadening of 0.1 eV. The ABS (gray, dashed line), constructed from INDO/S quantum-chemical excitation energies and oscillator strengths extracted from Ref. [93], is shown with a Lorentzian broadening of 0.1 eV.

(DFT+ U & TDDFT+ U) makes relatively little difference, and the effect of invoking the TDA is approximately that of a small, rigid blueshift. It is difficult to make a clear comparison against the large spread of experimental values, meanwhile. The agreement between the peak positions and line shapes (we do not attempt to compare physical magnitudes here) given by DFT & TDDFT+ U and INDO/S, both for EES and ABS, is remarkable, however, with the first bright energy agreeing to ~ 0.04 eV (albeit with a splitting in INDO/S that is absent in TDDFT+ U). The ABS peak positions are also in reasonable agreement with some of the experimental values given in Table II, though again interpretation is challenging here due to the spread of values. We now digress to consider these results.

TABLE II. Energies (in eV) of the singlet excitations of $\text{Ni}(\text{CO})_4$, as obtained without symmetry assignment from the peak positions of Fig. 12, with smaller peaks and shoulders removed. The coinciding peaks in Fig. 13 are assigned as optically bright excitations highlighted with a bold font.

| Method | | | | | | |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| DFT & TDDFT (PBE) | 4.26 | 4.50 | 4.67 | 4.75 | 5.17 | 5.27 |
| DFT+ U & TDDFT | 5.03 | 5.26 | 5.48 | 5.57 | 6.15 | 6.85 |
| DFT & TDDFT+ U | 3.63 | 3.91 | 4.03 | 4.19 | 4.38 | 4.75 |
| DFT+ U & TDDFT+ U | 4.72 | 4.91 | 5.02 | 5.39 | 5.45 | 5.59 |
| DFT+ U & TDDFT+ U (TDA) | 4.75 | 4.93 | 5.04 | 5.45 | 5.62 | 6.12 |
| Exp. (solvent) [91] | | 5.24 | 5.52 | 6.02 | | |
| Exp. (matrix) [92] | 4.54 | 5.17 | | | | |
| Exp. (gas) [93] | 4.5 | | 5.4 | 6.0 | | |
| INDO/S [93] | 3.93 | 3.98 | 4.05 | 4.15 | 4.36 | 4.39 |
| | 4.55 | 4.64 | 4.79 | 4.91 | 4.95 | 5.11 |
| | 5.29 | 5.36 | 5.71 | 6.20 | | |
| TDDFT (LDA) [95] | 4.36 | 4.60 | 4.62 | 4.70 | 4.82 | 4.95 |
| | 5.37 | 5.84 | 6.01 | | | |
| SAC-CI [101] | 4.52 | 4.53 | 4.79 | 4.97 | 5.25 | 5.41 |
| | 5.51 | 5.72 | 5.76 | 6.07 | 6.28 | |
| CASPT2 [94] | 3.58 | 3.72 | 4.04 | 4.34 | 4.88 | 5.14 |
| | 5.15 | 5.20 | 5.22 | 5.57 | 6.00 | 6.01 |

C. The use of a single Hubbard U parameter in DFT+ U and TDDFT+ U

The improvement of DFT & TDDFT by a first-principles Hubbard U correction to the *kernel* but not to the *potential*, if INDO/S can be taken as a benchmark, may be understood as a possible consequence of the following. The Hubbard U parameter is a measure of spurious interaction, one that is calculated as the derivative of an averaged potential that, in turn, is a measure of the derivative of an energy. On the one hand, therefore, U is well suited to measure the magnitude required for correction of the interaction kernel. On the other hand, it is not necessarily a good measure of the magnitude required for correction of the Kohn-Sham potential. More specifically, it has recently been shown by one of the present authors that very different parameters U_1 and U_2 may be needed for the constant and linear terms in the density, respectively, of the DFT+ U corrective potential [100]. Put another way, the linear and quadratic terms in Eq. (3) may benefit from different U_{eff} prefactors.

Dubbed DFT+ U_1+U_2 , this generalization of DFT+ U allows for the approximate enforcement of Koopmans' condition on the DFT+ U subspace, which is a condition that is implied by the assumptions underpinning the calculation of U . In other words, while the Hubbard U may successfully measure the self-interaction strength, and possibly open the correct fundamental gap via the quadratic energy term, a single parameter does not carry enough information to correctly

position the targeted subspace energetically with respect to the background (also known as bystander) states, a task for which the linear term is better equipped. Put yet another way, the double-counting correction used in the derivation of the contemporary DFT+ U functional is arguably too simple, for certain system types, and could gainfully be given its own separate premultiplicative parameter. The TDDFT+ U kernel does not suffer from this complication, however, since only the usual parameter associated with the quadratic energy term survives in the kernel. In this sense, contemporary methods for calculating a single U parameter may actually be better suited to TDDFT+ U than to DFT+ U . This is reflected by the apparent, paradoxical superior performance of DFT & TDDFT+ U over DFT+ U & TDDFT+ U in the aforementioned system Ni(CO) $_4$, albeit that this is a rather extreme test of DFT+ U insofar as the uncorrected PBE functional already performs well, and the relevant subspace is very far from half-filling.

Indeed, any ill effects of conventional DFT+ U on the potential are expected to be most strongly felt when applying DFT+ U to spin-unpolarized $3d$ spaces that are almost full (or empty) such as in Ni(CO) $_4$, since then the conduction (or valence) band edge is of predominantly background-orbital character. The Kohn-Sham gap is neither of $3d \rightarrow 3d$ character nor reliably determined by the familiar U in such cases. A workaround alternative (albeit not equivalent) to DFT+ U_1+U_2 may be the application of DFT+ U to other orbital types, e.g., O $2p$, C $2p$, and possibly Ni $4s$, but this has not been explored in the present work. A complete counterexample to this, where DFT+ U is very effective, is next provided by an open-shell complex, where the Kohn-Sham gap is strongly affected by a varying Hubbard U parameter.

V. FIRST-PRINCIPLES SPECTRA OF A HIGH-SPIN COBALT-CENTERED COMPLEX

CoL $_2$ Cl $_2$ ($L = 2$ -aminopyrimidine: C $_4$ H $_5$ N $_3$) is a Co-centered, distorted pseudo-tetrahedral complex with two types of ligands, as illustrated in Fig. 14. The central Co atom has a nominal charge of 2+, with a $3d$ subshell containing 7 electrons. Cl $^-$ is a π -donor weak-field ligand, which leads to a splitting of the $3d$ subshell of the Co atom into a high-spin configuration in a pseudo-tetrahedral symmetry [98,102]. In its high-spin configuration, the $3d$ orbitals at higher energies contain unpaired electrons, resulting in a total spin of $3\mu_B$. The fully and partially filled molecular orbitals at higher energies are predominantly hybrids comprised of Co $3d$ and Cl $3p$ orbitals. Moreover, further splitting of the energy levels by $3d$ - $3p$ hybridization occurs by means of the distortion due to the tilted L -ligands. The low-lying excitations are expected to have strong $3d \rightarrow 3d$ character in this molecule.

Experimental values for the low-lying, spin-allowed optically bright excitations of CoL $_2$ Cl $_2$ are presented in Table III. Also provided are prior predictions from high-level quantum-chemistry methods, i.e., complete active space self-consistent field (CASSCF) and CASSCF improved further by second-order N -electron valence perturbation theory (NEVPT2) [103–106], which were extracted from Ref. [107]. Our own TDDFT calculations invoke the TDA for this spin-polarized system, due to technical limitations of the

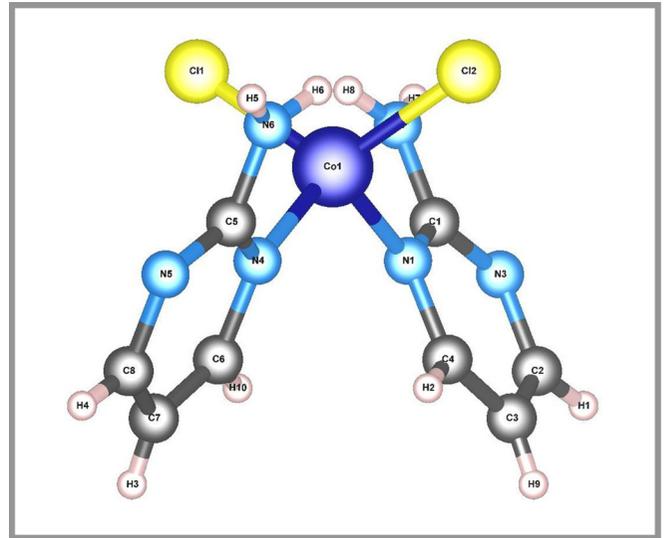


FIG. 14. The molecular structure of CoL $_2$ Cl $_2$ ($L = 2$ -aminopyrimidine: C $_4$ H $_5$ N $_3$).

implementation. Two different first-principles effective parameters were tested in our DFT+ U and TDDFT+ U calculations, and these were generated following the procedures described in detail in Ref. [43]. Briefly, the like-spin $U_{\text{eff}} = U - J$ results from a treatment of the spin channels as forming an effective two-site model in the “scaled 2×2 ” method, and this is expected to yield results (in this case 5.724 eV) comparable to those from any correct method that separately calculates the Hubbard U and Hund’s J . The less canonical

TABLE III. Energies (in eV) of the singlet excitations of CoL $_2$ Cl $_2$, as obtained without symmetry assignment from the peak positions of Fig. 15(a), with smaller peaks and shoulders removed. Coinciding peaks in Fig. 15(b) are assigned as optically bright excitations, highlighted with a bold font. Experimental peak energies extracted from Ref. [107] are accurate to the nearest 0.05 eV, approximately.

| Method | | | | | |
|--|-------------|-------------|-------------|-------------|-------------|
| DFT & | 1.19 | 1.38 | 1.74 | 1.94 | 2.04 |
| TDDFT (TDA) | 2.28 | 2.68 | 2.92 | | |
| $U_{\text{eff}} = 5.724 \text{ eV}$ (scaled 2×2 [43]) | | | | | |
| DFT+ U & | 2.80 | 2.99 | 3.24 | 3.31 | 3.49 |
| TDDFT (TDA) | | | | | |
| DFT+ U & | 1.35 | 1.41 | 1.80 | 2.12 | 2.86 |
| TDDFT+ U (TDA) | 2.99 | 3.08 | | | |
| $U_{\text{eff}} = 3.798 \text{ eV}$ (averaged 1×1 [43]) | | | | | |
| DFT+ U & | 2.16 | 2.45 | 2.71 | 2.85 | 2.98 |
| TDDFT (TDA) | 3.06 | | | | |
| DFT+ U & | 0.20 | 0.35 | 0.56 | 0.90 | 1.02 |
| TDDFT+ U (TDA) | 2.64 | 2.85 | 2.93 | 3.00 | |
| Expt. (solvent) [107] | 1.10 | 2.00 | 2.15 | 2.45 | |
| CASSCF [107] | 0.35 | 0.43 | 0.56 | 0.72 | 0.87 |
| | 1.06 | 2.76 | 2.80 | 2.84 | |
| CASSCF | 0.49 | 0.58 | 0.75 | 0.95 | 1.13 |
| + NEVPT2 [107] | 1.36 | 2.67 | 2.72 | 2.75 | |

“averaged 1×1 ” method calculates the like-spin U_{eff} as the average of the U parameters calculated individually for the two spin channels when decoupled (each forming part of the bath for the other), and it may be a more reasonable assumption when an explicit J correction term is not used (as in the present work, where $U_{\text{eff}} = 3.798$ eV).

In Fig. 15(a), we see that DFT+ U & TDDFT push excitation features at lower energies higher, compared to DFT+ U & TDDFT, by ~ 1.6 – 2.0 eV (~ 1.0 eV) in the 2×2 (1×1) case. In both cases, an aggregate of excitations forms at ~ 2.8 eV, and in neither case does DFT+ U & TDDFT provide a promising agreement with prior experiment or CASSCF-based results. Meanwhile, the alternate combination, DFT & TDDFT+ U , which performed rather well in the case of $\text{Ni}(\text{CO})_4$, was found to be not at all viable here, for either U_{eff} value, as it gives rise to unphysical, negative-valued excitation energies (a single instability). The interaction of DFT+ U & TDDFT+ U in this system is nontrivial, and the net result cannot be well described as a linear combination (a cancellation) of the two method’s effects, in general. The linear combination picture holds to a greater degree for the *higher*-valued, more canonical (2×2) prescription for U_{eff} , counterintuitively. With this, we find that uncorrected DFT & TDDFT does a better job of reproducing the experimental absorption curve in Fig. 15(b), and that the absent low-lying, tightly bound exciton features predicted by CASSCF are no better recovered. Here, referring to Fig. 15(b), we emphasize that all curves are independently normalized so that their maximum peak reaches a value of unity, and that it is not necessarily the case that DFT & TDDFT recovers the experimental maximum absorption cross section by any means.

Conversely, with the lower-valued (1×1) prescription for U_{eff} , we find that the linear combination picture breaks down completely. With this U_{eff} , it appears that the effect of DFT+ U is insufficient to eradicate the strong $3d \rightarrow 3d$ character of the low-lying excitations. Then, when TDDFT+ U is applied on top of this, a very strong exciton rebinding effect (of ~ 2.0 eV) occurs, yielding a net exciton binding effect of ~ 1.0 eV with respect to DFT & TDDFT. Ultimately, DFT+ U & TDDFT+ U within the 1×1 prescription for U_{eff} does yield a group of tightly bound ligand-field excitations that can be said to be in qualitative agreement with the CASSCF predictions of Ref. [107]. The accuracy improvements for lower-energy excitations offered by DFT+ U & TDDFT+ U are seen in Table III. Specifically, both DFT & TDDFT and DFT+ U & TDDFT fail to capture the lowest threefold-degenerate excitation (highlighted with light pink) between ~ 0.50 and 0.75 eV predicted at the level of CASSCF+NEWPT2. Moreover, DFT+ U & TDDFT also overestimates the second group of threefold-degenerate excitations (highlighted with light blue) at around ~ 0.90 – 1.40 eV, either when compared against the experimental value of 1.12 eV or the CASSCF+NEWPT2 prediction of ~ 0.95 – 1.13 eV. DFT+ U & TDDFT+ U determines the lowest optically bright excitation energy with a relatively high accuracy at 0.56 eV, comparing to both CASSCF and CASSCF+NEWPT2. Furthermore, it performs well by locating the second group of threefold-degenerate excitations (highlighted with light blue) at 0.90 and 1.02 eV. However, DFT+ U & TDDFT performs better, without a doubt, for the third group of threefold-degenerate excitations

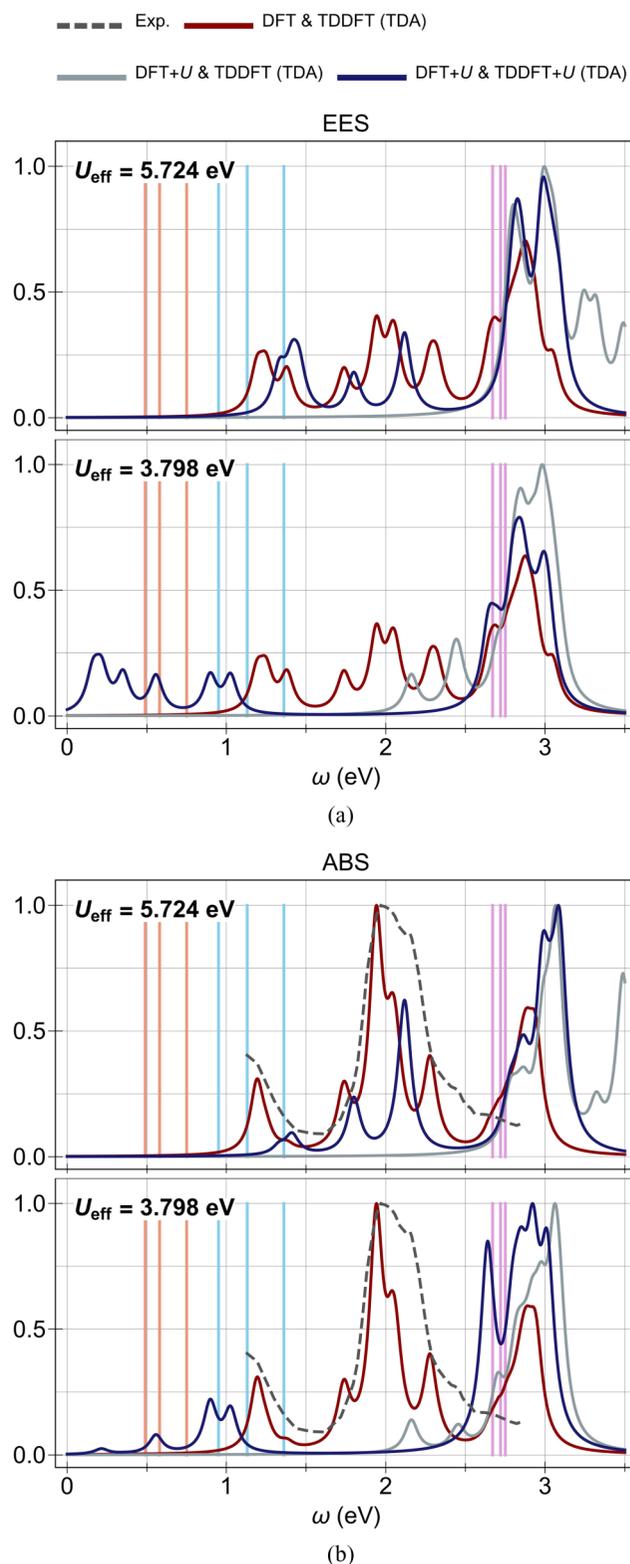


FIG. 15. The singlet EES and ABS of CoL_2Cl_2 calculated using first-principles like-spin Hubbard U_{eff} values calculated as described in Appendix B, shown with a Lorentzian broadening of 0.1 eV. The experimental absorption spectrum (gray, dashed line) was extracted from Ref. [107] and scaled by setting the global peak to unity. The optically bright excitation energies calculated using CASSCF+NEWPT2 in Ref. [107] are shown in the form of vertical lines with colors matching their values presented in Table III.

(highlighted with light purple) at 2.45 eV, when comparing to the experimental value. Overall, we can conclude that first-principles (1×1 prescription) DFT+ U & TDDFT+ U performs better for low-lying excitations than DFT & TDDFT, but this comes at the expense of completely removing the prominent absorption peak at ~ 2.0 eV where experiment and DFT & TDDFT agree. None of the available methods (including CASSCF), therefore, offer reliable correction of the spectra for both $3d \rightarrow 3d$ and higher-energy excitations, and this is as expected given the spatially localized nature of Hubbard U corrections when applied to metal $3d$ orbitals only.

VI. CONCLUSION

In this work, we carried out a systematic investigation of the extension of Hubbard U corrected approximate Kohn-Sham DFT to the excited-state regime, namely TDDFT+ U . For this, a linear-scaling, linear-response implementation of TDDFT+ U was developed within the ONETEP code by combining existing linear-scaling DFT+ U [44,45], conduction-band optimization [89], and beyond Tamm-Dancoff TDDFT [69–71] methods. Our implementation has allowed us to decouple and analyze the separate and combined effects of Hubbard U correction at the DFT (potential) and TDDFT (kernel) levels, offering insights into the performance and potential range of useful applicability of TDDFT+ U . A four-level toy model has proved invaluable to our interpretation of TDDFT+ U and the numerical results that support this picture, particularly in two representative low-spin (spin-unpolarized but nonisoelectronic) Ni-centered complexes. In these systems, we first treated the Hubbard U as a free parameter in order to understand in detail the exciton binding effect of TDDFT+ U , as well as the tendency for the effects of DFT+ U and TDDFT+ U to approximately cancel. We also analyzed in detail the differing effects of Hubbard U on TDDFT depending on whether the Tamm-Dancoff approximation is invoked. Including also a challenging Co-centered open-shell, high spin coordination complex, we calculated first-principles Hubbard U and Hund's J parameters for all three systems, following the spin-polarized, minimum-tracking [108] linear-response approach introduced in Ref. [43]. This has enabled us to generate fully first-principles excitation and absorption spectra for each of these elusive systems and to compare with prior experimental and quantum chemical findings.

Physically, our analysis shows that TDDFT+ U can be thought of as a self-interaction correction for excitons, acting to enhance the exciton binding. Indeed, quite apart from TDDFT+ U being mandated in principle when TDDFT is applied upon a DFT+ U Kohn-Sham eigensystem, we find that TDDFT+ U can be very effective in rebinding well-defined strongly localized, optically dark ligand-field excitations. The Hubbard U dependence of this rebinding is illustrated nicely, we think, in Fig. 5(c). Our study has identified examples of such ligand-field excitations that are predicted at low energies by quantum-chemistry methods but pushed to unrealistically high energies by first-principles DFT+ U . TDDFT+ U can address this effectively, to some extent, but only if the localized

character of those excitations has not already been eradicated by DFT+ U , however, as illustrated in Fig. 15(a). In general, while DFT+ U shifts excitation energies of transitions into, out of, and within the targeted localized subspace by modifying the underlying Kohn-Sham energy levels in proportion to the effective Hubbard U parameter, approximately speaking, TDDFT+ U only directly affects transitions *within* that subspace. This gives rise to an incomplete cancellation of the effects of DFT+ U and TDDFT+ U , and as a result we conclude that while the combination of DFT+ U and TDDFT+ U may often give rise to something of a linear combination of the two method's effect, the interaction between them may also be nontrivial, with multiple U -dependence regimes potentially emerging.

Existing approaches for calculating the adiabatic limit of the Hubbard U and Hund's J within DFT (or more precisely generalized Kohn-Sham DFT, in practice), such as the linear-response method, already calculate the necessary parameters for TDDFT+ U by construction. Indeed, our results suggest that these parameters may be *more* suited to TDDFT+ U than to DFT+ U , in the sense that U (and J) exists at the same energy-derivative order as the kernel correction $f_U^{\sigma\sigma'}$, whereas the DFT+ U correction to the potential retains a somewhat arbitrary constant (in the sense that a choice of double-counting correction must be made). Furthermore, our results add to the growing body of literature that suggests that DFT+ U should be used with caution on closed-shell, or more generally low-spin systems, as discussed in Ref. [43] and references therein. Our findings on the closed-shell complex Ni(CO)₄, for example, where DFT & TDDFT+ U performs rather well when judged against the INDO/S quantum-chemistry method (see the third panel of Fig. 13), suggest a basic failure of the DFT+ U corrective potential in combination with the first-principles $U_{\text{eff}} = U - J$.

An interesting avenue for future investigation in problematic systems such as those studies is the use of a second Hubbard U parameter to enforce Koopmans' condition to the targeted subspace [100], as discussed in Sec. IV C. This idea effectively fixes the arbitrary constant in DFT+ U , or locates the double-counting correction from first principles, but its effect in nontrivial systems is yet to be investigated. Overall, notwithstanding, a picture emerges in the present work whereby the application of Hubbard U correction to a single localized subspace alone (with first-principles parameters [43]) may be advantageous and expedient for the qualitative description of optically dark $3d \rightarrow 3d$ excitations that are difficult to otherwise recover. This description can come, however, at the expense of considerably worsening the description of less localized excitations that are well described by standard, semilocal approximations to TDDFT. Further research is warranted, therefore, on generalizations to the contemporary DFT+ U functional such as to incorporate further chemical information. More basically, perhaps, but no less interestingly, more research is needed on the effects of DFT+ U , DFT+ U + J [33], and DFT+ U + V [109] (and their potential respective TDDFT+ U extensions) to more delocalized subspaces centered on ligand atoms (see, for example, the oxygen $2p$ treatment in Ref. [43]) or even bond-centered ones.

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APPENDIX A: COMPUTATIONAL DETAILS

First-principles simulations were performed using our implementation of the TDDFT+ U method in the ONETEP linear-scaling package [45,86,87]. All calculations used the Perdew-Burke-Ernzerhof (PBE) [7] generalized gradient approximation as the underlying exchange-correlation functional. Norm-conserving scalar-relativistic PBE pseudopotentials were generated in-house for neutral Ni, Cl, O, C, N, H, and Co^{2+} using the OPIUM code [110]. Ground-state simulations are referred to here as *single-point* (SP), and the subsequent procedure of variationally optimizing the second set of NGWFs to represent the unoccupied manifold [89] is referred to as *conduction* (COND). Initial ionic geometries were adopted from a prior first-principles study [111] in the case of $\text{Ni}(\text{CN})_4^{2-}$, and from experimental data [112] in the case of $\text{Ni}(\text{CO})_4$. These molecular geometries were optimized iteratively until they fulfilled three convergence criteria: on the maximum atomic displacements ($0.005a_0$), total energy per atom (10^{-6} Ha), and total atomic force (0.002 Ha/ a_0), by means of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [113,114]. In the case of CoL_2Cl_2 , the molecular geometry was directly adopted from Ref. [115] for the sake of preserving with comparability the spectra of Ref. [107], where the authors used the same geometry. The molecules were then positioned into smaller cuboidal simulation boxes centered on their respective metallic atoms, with the available minimum dimensions needed to satisfy the requirements of the Martyna-Tuckerman periodic boundary correction (PBC), which was applied with its dimensionless parameter set to 7 as recommended in Ref. [116].

A series of convergence tests were performed to safeguard the quality of excited-state simulations, while maintaining a reasonable computational cost at the SP, COND, and TDDFT levels (recalling that the effective U is treated as a parameter, which significantly multiplies the total computational demand of the study). The resulting common set of parameters used in this study is summarized in Table IV. The effective plane-wave kinetic energy cutoff (E_{cut}) and the cutoff radius (R_{NGWFs}) of the variationally optimized nonorthogonal generalized Wannier functions NGWFs, a minimal basis generated by ONETEP, were converged at values of 1200 eV and $12a_0$, respectively, yielding an energy error per atom within 1 meV in SP calculations. The value of R_{NGWF} was separately tested in COND calculations and found to be adequate for describing the virtual orbital eigenenergies. A total of 9(18) spin-degenerate NGWFs were used for Ni atoms in order to complete the period up to Kr, and a total of 4 NGWFs

TABLE IV. The converged run-time parameters used for $\text{Ni}(\text{CN})_4^{2-}$, $\text{Ni}(\text{CO})_4$, and CoL_2Cl_2 . Here, E_{cut} is the kinetic energy cutoff, R_{NGWF} is the atom-centered nonorthogonal generalized Wannier function (NGWF) spherical cutoff radius, and N_{NGWF} is the number of NGWFs per atom to be variationally optimized *in situ*.

| Parameter | Stage | Value |
|-------------------------------|-----------|---------|
| E_{cut} | All | 1200 eV |
| R_{NGWF} | All | $12a_0$ |
| $N_{\text{NGWF}}^{\text{Ni}}$ | SP (COND) | 9 (18) |
| $N_{\text{NGWF}}^{\text{Co}}$ | SP (COND) | 9 (18) |
| $N_{\text{NGWF}}^{\text{Cl}}$ | SP (COND) | 4 (13) |
| $N_{\text{NGWF}}^{\text{C}}$ | SP (COND) | 4 (8) |
| $N_{\text{NGWF}}^{\text{N}}$ | SP (COND) | 4 (8) |
| $N_{\text{NGWF}}^{\text{O}}$ | SP (COND) | 4 (8) |
| $N_{\text{NGWF}}^{\text{H}}$ | SP (COND) | 1 (2) |

for each of C, O, and N were used to complete the period up to Ar. These were optimized at the SP (COND) level in our Ni-centered complexes, whereas for the Co-centered complex 9 (18), 4 (13), 4 (8), and 1 (2) NGWFs, they were variationally optimized for Co, Cl, C, N, and H atoms during SP (COND) simulations. As CoL_2Cl_2 is an open-shell system, spin-polarized calculations were performed with a fixed total spin of $3\mu_B$, and the initial configuration of Co for the pseudoatomic solver (which affects both the NGWF initial guess and the $3d$ pseudo-orbitals defining the DFT+ U subspace) was set to the theoretical high-spin configuration of $[\text{Ar}]4s^03d^7$, with a $3\mu_B$ total spin. The occupied-unoccupied Kohn-Sham eigenvector product spaces were constructed by using full valence manifolds, which are represented by 24 and 25 spin-degenerate NGWFs in $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Ni}(\text{CO})_4$, respectively, and 49 and 46 NGWFs for spin-up and spin-down, respectively, in CoL_2Cl_2 . For the conduction manifolds, 20 (10 per spin channel), 16 (8 per spin channel), and 11 (4 for up and 7 for down) KS conduction orbitals were optimized in $\text{Ni}(\text{CN})_4^{2-}$, $\text{Ni}(\text{CO})_4$, and CoL_2Cl_2 , respectively. These parameters were selected on the basis of KS eigenvalues, providing sufficiently many bound states for the targeted spectral range in TDDFT calculations. The first 50 singlet excitations for Ni-centered complexes and 20 singlet excitations for CoL_2Cl_2 were calculated by variational minimization, within the larger valence-conduction product space spanned by the optimized NGWF basis. We do not place a strong emphasis on the higher-energy excitations shown in our plots, being more interested and confident in the lower-energy excitations affected by the Hubbard U correction. In particular, in many of our figures the EES and ABS appear gapped at high energy, but this is nothing more than an artefact of the limited number of excitations calculated.

APPENDIX B: FIRST-PRINCIPLES CALCULATION OF HUBBARD U AND J PARAMETERS USING THE MINIMUM-TRACKING LINEAR-RESPONSE METHOD

The efficiency and robustness of the DFT+ U (+ J) method is essentially dependent on the determination of the Hubbard parameters. A common approach is to use linear response to

TABLE V. Hubbard and Hund parameters (in eV) calculated using the scaled 2×2 method of Ref. [43].

| Interaction | Ni(CN) $_4^{2-}$ | Ni(CO) $_4$ |
|--|------------------|---------------|
| $f^{\sigma\sigma}, f^{\sigma\bar{\sigma}}$ | 6.901, 8.456 | 9.849, 11.388 |
| U, J | 7.678, 0.777 | 10.618, 0.769 |
| U_{eff} | 6.901 | 9.849 |

determine them [27,32]. In this work, we employ the recently introduced minimum-tracking variant of linear response as implemented in the ONETEP code [108], and in particular its spin-polarized extension introduced in Ref. [43]. In this, the “scaled 2×2 ” method can be used to evaluate the Hubbard U , Hund’s J , and effective Hubbard U parameter ($U_{\text{eff}} = U - J$) for all three systems using the formulas

$$U = \frac{1}{2} \frac{\lambda_U (f^{\uparrow\uparrow} + f^{\uparrow\downarrow}) + f^{\downarrow\uparrow} + f^{\downarrow\downarrow}}{\lambda_U + 1}, \quad (\text{B1})$$

$$J = -\frac{1}{2} \frac{\lambda_J (f^{\uparrow\uparrow} - f^{\downarrow\uparrow}) + f^{\uparrow\downarrow} - f^{\downarrow\downarrow}}{\lambda_J - 1}, \quad (\text{B2})$$

where

$$\lambda_U = \frac{\chi^{\uparrow\uparrow} + \chi^{\uparrow\downarrow}}{\chi^{\downarrow\uparrow} + \chi^{\downarrow\downarrow}} \quad \text{and} \quad \lambda_J = \frac{\chi^{\uparrow\uparrow} - \chi^{\uparrow\downarrow}}{\chi^{\downarrow\uparrow} - \chi^{\downarrow\downarrow}}. \quad (\text{B3})$$

The spin-dependent interaction strengths $f^{\sigma\sigma'}$ are calculated by incrementally varying subspace-uniform perturbing potentials $\delta v_{\text{ext}}^\sigma$, relaxing fully to the ground state on each step, and then measuring the resulting small changes in the subspace occupancies n^σ and subspace-averaged Kohn-Sham potentials v_{KS}^σ . The projected interacting response matrices are given by $\chi^{\sigma\sigma'} = dn^\sigma / dv_{\text{ext}}^{\sigma'}$. When the interaction strengths $f^{\sigma\sigma'}$ are calculated using a 2×2 matrix equation indexed by spin, we arrive at the “scaled 2×2 ” model, which reproduces conventional formulas for U and J . Indeed, for spin-unpolarized systems such as the Ni-centered complexes studied in this

TABLE VI. Hubbard and Hund parameters (in eV) calculated using the scaled 2×2 (top panel) and the averaged 1×1 methods (bottom panel) of Ref. [43] for CoL $_2$ Cl $_2$.

| Interaction | CoL $_2$ Cl $_2$ |
|--|------------------|
| $f^{\uparrow\uparrow}, f^{\downarrow\downarrow}$ | 13.711, 15.268 |
| $f^{\downarrow\uparrow}, f^{\uparrow\downarrow}$ | 7.650, 6.029 |
| λ_U, λ_J | -0.039, -0.195 |
| U, J | 6.529, 0.805 |
| U_{eff} | 5.724 |
| U^\uparrow, U^\downarrow | 3.503, 4.093 |
| U_{eff} | 3.798 |

work, $\lambda_U = 1$ and $\lambda_J = -1$, and as a result we have $U = (f^{\sigma\bar{\sigma}} + f^{\sigma\sigma})/2$, $J = (f^{\sigma\bar{\sigma}} - f^{\sigma\sigma})/2$, and, simply but reassuringly, $U_{\text{eff}} = f^{\sigma\sigma}$.

When spin-off-diagonal elements are neglected, instead, we have the “averaged 1×1 ” model, in which $U_{\text{eff}} = (U^\uparrow + U^\downarrow)/2$, where $U^\sigma = d(v_{\text{KS}}^\sigma - v_{\text{ext}}^\sigma)/dn^\sigma$. This model effectively decouples the spin populations into distinct sites, reflecting the form of the canonical DFT+ U functional. Each spin channel, for a given localized subspace, then forms part of the screening bath for the other, and the effects of Hund’s J are then already incorporated into U_{eff} at an approximate level.

In practice, a discrete logarithmic grid of perturbation strengths, $\{-0.10, -0.01, 0.00, 0.01, 0.10\}$ eV, was used in this work to calculate the U and J parameters, resulting in excellent linear fits. For the spin-unpolarized Ni-centered complexes, it was necessary only to perturb one spin channel, since half of the spin-indexed matrix elements could be filled using symmetry. The resulting parameters are summarized in Table V.

As CoL $_2$ Cl $_2$ is a spin-polarized system, the responses of each spin channel were measured by perturbing the respective spin channels, separately, one at a time. The resulting first-principles parameters for the Co $3d$ subspace are summarized in Table VI.

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