Electronic structure of rare-earth mononitrides: quasiatomic excitations and semiconducting bands
Anna Galler, Leonid Pourovskii

To cite this version:
Anna Galler, Leonid Pourovskii. Electronic structure of rare-earth mononitrides: quasiatomic excitations and semiconducting bands. New Journal of Physics, 2022, 24 (4), pp.043039. 10.1088/1367-2630/ac6317. hal-04452828

HAL Id: hal-04452828
https://hal.science/hal-04452828
Submitted on 12 Feb 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution 4.0 International License
Electronic structure of rare-earth mononitrides: quasiatomic excitations and semiconducting bands

To cite this article: Anna Galler and Leonid V Pourovskii 2022 New J. Phys. 24 043039

View the article online for updates and enhancements.

You may also like

- Non-equilibrium electronic transport through a quantum dot with strong Coulomb repulsion in the presence of a magnetic field
  Denis Zhuravel, Dmitry V Anchishkin, Roland Hayn et al.

- An exact sum-rule for the Hubbard model: an historical/pedagogical approach
  S Di Matteo and Y Claveau

- Sub-gap Fano resonances in a topological superconducting wire with on-site Coulomb interactions
  Piotr Stefaski
Electronic structure of rare-earth mononitrides: quasiatomic excitations and semiconducting bands

Anna Galler1,∗ and Leonid V Pourovskii2,3

1 Institute of Solid State Physics, TU Wien, Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria
2 Centre de Physique Théorique, Ecole Polytechnique, CNRS, Institut Polytechnique de Paris, 91128 Palaiseau Cedex, France
3 Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France

∗ Author to whom any correspondence should be addressed.
E-mail: galler.anna@gmail.com

Keywords: rare-earth semiconductors, electronic correlations, first-principles methods

Abstract

The electronic structure of the rare-earth mononitrides LnN (where Ln = rare-earth), which are promising materials for future spintronics applications, is difficult to resolve experimentally due to a strong influence of defects on their transport and optical properties. At the same time, LnN are challenging for theory, since wide semiconducting 2p and 5d bands need to be described simultaneously with strongly correlated 4f states. Here, we calculate the many-body spectral functions and optical gaps of a series of LnN (with Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er) by a density-functional + dynamical mean-field theory (DFT + DMFT) approach treating the correlated Ln 4f shells within the quasi-atomic Hubbard-I approximation. The on-site Coulomb interaction in the 4f shell is evaluated by a constrained DFT + Hubbard-I approach. Furthermore, to improve the treatment of semiconducting bands in DFT + DMFT, we employ the modified Becke–Johnson semilocal exchange potential. Focusing on the paramagnetic high-temperature phase, we find that all investigated LnN are pd semiconductors with gap values ranging from 1.02 to 2.14 eV along the series. The pd band gap is direct for light Ln = La...Sm and becomes indirect for heavy rare-earths. Despite a pronounced evolution of the Ln 4f states along the series, empty 4f states are invariably found above the bottom of the 5d conduction band. The calculated spectra agree well with those available from x-ray photoemission, x-ray emission and x-ray absorption measurements.

1. Introduction

The mononitrides LnN (where Ln is a lanthanide element) represent a rare case of ferromagnetic semiconductors [1–5] standing out among other lanthanide pnictides, which are generally antiferromagnets [6]. In the ferromagnetic state, both the top of the valence and bottom of the conduction band in LnN are expected to be of majority-spin character resulting in a complete spin polarization of hole and electron carriers [3]. The mononitride series is thus promising for spintronics applications [7, 8]. It has attracted a renewed interest recently, especially from the experimental side, with detailed measurements of the optical conductivity in NdN [4], SmN [9, 10] and DyN [5], quantitative studies of the effects of nitrogen vacancies in SmN [11] and DyN [5] and attempts to reconstruct the band structure of NdN [4] and SmN [9] from optical measurements.

Even if the LnN compounds have been studied both experimentally and theoretically for several decades, there still exist numerous ambiguities regarding their electronic structure, transport and magnetic properties. Experimental investigations are often hindered by difficulties in fabricating good stoichiometric samples free of oxygen impurities and nitrogen vacancies. Each nitrogen vacancy is predicted to dope two electrons to the conduction band with the third one forming a state in the gap [12]. Apparently, due to the effect of vacancies, earlier transport measurements on LnN samples often reported a metallic behavior [13–15]. With progress in the fabrication of high-quality LnN films by pulsed laser deposition and...
molecular beam epitaxy, the semiconducting nature of several LnN has been established, including GdN [1, 16], NdN [17], SmN [18] and DyN [5, 18]. Separating out the effect of defects remains, however, an outstanding issue. Vacancy-induced levels within the pd gap can be difficult to distinguish from sharp 4f states resulting in conflicting reports on the nature of states forming the bottom of the conduction band in NdN, SmN, and DyN [4, 5, 9, 10, 19, 20]. In addition, LnN are prompt to rapid oxidation, hence, most of recent investigations are carried out on LnN thin films grown on semiconducting substrates and protected by capping layers [3]. Intrinsic properties of bulk stoichiometric LnN are thus hard to access experimentally.

In view of these difficulties, there have been numerous ab initio studies aimed at establishing the electronic structure of pristine LnN. First band structure calculations of Gd-pnictides were carried out already in the 70s [21]. However, density-functional theory (DFT) in conjunction with the standard local density approximation (LDA) or generalized-gradient approximation treatments of exchange and correlation effects has a well-known tendency to underestimate band gaps in semiconductors. In addition, Ln 4f electrons exhibit strong local correlation effects that are beyond standard DFT approaches. Hence, a first overarching study of the electronic structure of the entire series of rare-earth mononitrides LnN (Ln = Ce...Yb) by Aerts et al [22] employed a self-interaction corrected (SIC) approach to take into account the localized nature of the Ln 4f states. This study predicted a broad range of electronic properties along the series, from half-metallic to insulating. Another comprehensive study of the LnN electronic structure was performed by Larson et al [23] employing DFT with +U correction applied to Ln 4f. Since a magnetic order needs to be assumed in DFT + U to open the Mott gap, the paramagnetic electronic structure was derived by averaging over spin up and down contributions. With the Hubbard U applied to the Ln 4f states only, DFT + U predicted half-metallic states for the LnN series [23]. In order to correct the underestimated semiconducting pd gap, references [23, 24] introduced a + U term also for the empty 5d shell, for which it amounts to an upward shift of the 5d states by the double-counting term. Though this shift can indeed correct the gap in an ad hoc way, the underlying physics of nonlocal exchange opening the semiconducting band gap is not captured by this approach.

The electronic structure of ferromagnetic LnN were subsequently calculated using more advanced approaches to nonlocal exchange—hybrid functionals and the GW method. Employing the hybrid functional B3LYP, reference [25] predicted a half-metallic ground state for ferromagnetic GdN, while another hybrid functional (HSE) calculation [26] obtained for the same compound a semiconducting band structure with a miniscule gap for the majority spin. Chantis et al [27] applied a quasi-particle self-consistent GW (QSGW) approach to various rare-earth monopnictides including GdN in the ferromagnetic state. They obtained a direct gap of 0.46 eV for majority and 1.48 eV for minority spin, which upon spin averaging agrees reasonably with the optical gap of 1.31 eV measured in experiment. However, strong electronic correlations on localized 4f shells are a difficult case for weak-coupling perturbative approaches such as GW. Indeed, the QSGW calculations overestimate the splitting between the occupied and unoccupied rare-earth 4f states with an upper Hubbard band (UHB) lying significantly higher in energy compared to DFT + U calculations. The same problem regarding the treatment of 4f states was observed in reference [28], where the QSGW approach has been applied to DyN, GdN and HoN.

Strong local correlations on 4f shells can be adequately described within the non-perturbative DMFT approach [29, 30]. The combination of DFT with DMFT [31], abbreviated as DFT + DMFT, has been applied to numerous correlated materials [32, 33] including rare-earth metals [34], monopnictides [35, 36] and monochalcogenides [37]. These works on lanthanide compounds employed the quasi-atomic Hubbard-I approximation [38] neglecting hybridization of the 4f states in the DMFT impurity problem. This DFT + Hubbard-I approach is well suited to address compounds with quasi-atomic rare-earth 4f shells, where it is able to capture multiplet effects absent in effective one-electron methods such as DFT + U. The Hubbard-I approximation is, instead, less suited to address 4f shells in compounds involving Ce, Eu and Yb since they tend to show mixed-valence behavior. In contrast to effective one-electron methods, DFT + Hubbard-I is able to properly describe 4f localization in the paramagnetic state. It is known from experiment that most LnN exhibit ferromagnetic order at low temperatures [1–5]. However, their Curie temperatures are quite low—with a maximum $T_C = 68$ K for GdN [16]—so that at room temperature they are actually all paramagnets.

Merits and drawbacks of various approaches (standard DFT, DFT + U, DFT + Hubbard-I) for TbN have been evaluated by reference [36]. While only DFT + Hubbard-I is able to capture the expected atomic multiplets, none of the employed approaches predicts a semiconducting gap, as apparent from the computed metallic spectral functions [36]. This is due to the fact that DFT + Hubbard-I includes only local electronic correlations, so it does not improve on the underestimation of semiconducting band gaps. Thus, previous theoretical works on LnN either corrected the semiconducting pd gap by employing advanced approaches to non-local exchange or included local correlations on the 4f shells within a DMFT framework. A comprehensive first principles study of LnN taking into account both effects is still lacking.
In the present paper we tackle this problem by calculating the electronic structure of the LnN series using an *ab initio* method that includes nonlocal exchange through the modified Becke–Johnson (mBJ [39, 40]) exchange potential while local 4f correlations are simultaneously included with DMFT in the Hubbard-I approximation. The on-site Coulomb repulsion $U$ for 4f shells is calculated by a constrained DFT + Hubbard-I technique, which we describe in detail in the methods section. This methodology termed mBJ + Hubbard-I has very recently been applied to the rare-earth fluoro sulfides LnSF [41] and rare-earth sesquioxides Ln$_2$O$_3$ [42]. Here, we focus on the paramagnetic phase of LnN, which has been scarcely explored in previous theoretical works, and analyze in detail the evolution of the LnN electronic structure along the series.

The structure of the article is the following: first, we outline our computational mBJ + Hubbard-I framework in section 2, with a particular focus on the *ab initio* computation of the screened Coulomb interactions $U$ within a constrained DFT + Hubbard-I approach. Our results, including an overview of computed optical gaps and $\mathbf{k}$-integrated spectral functions for all investigated LnN from PrN to ErN, are described in section 3. In particular, our analysis is focused on several compounds—NdN, SmN, TbN and HoN—that have been subject to intensive discussions in the recent literature. Our conclusions are presented in section 4.

2. Methods

2.1. The mBJ + Hubbard-I approach

We start from a charge-self-consistent DFT + DMFT calculation [43–47] of the target rare-earth mononitrides LnN (Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er). All these compounds have localized Ln 4f shells, hence the quasi-atomic Hubbard-I approximation can be employed as DMFT impurity solver. In rare-earth semiconductors, corrections to the Hubbard-I solution due to hybridization effects are most significant for occupied 4f states located inside the semiconducting $pd$ gap [42]; this situation does not occur in the LnN systems we consider. Since hybridization corrections are expected to be small otherwise [41, 42], we neglect them in the present work.

We construct projective Wannier functions [44] to represent the subspace of the correlated Ln 4f states using the Kohn–Sham (KS) eigenstates enclosed by an energy window $[-9.5:13.6]$ eV around the Fermi level. We employ a fully rotationally-invariant screened Coulomb interaction in our calculations.

After convergence of the self-consistent DFT + Hubbard-I calculations, we run an additional DFT cycle employing the Tran–Blaha mBJ potential [39, 40], as implemented in the wien2k [43] program package. Such a perturbative use of the mBJ potential is appropriate since, strictly speaking, the mBJ potential is not in the atomic limit [49], i.e.

$$\Sigma_{DC} = U(N - 0.5) - J(0.5N - 0.5)$$

with the corresponding Ln$^{+}$ nominal atomic occupancies $N$. The chosen double-counting correction is orbitally-independent since a perturbative use thereof can yield more reliable values for semiconducting band gaps [48]. For more details regarding our mBJ + Hubbard-I approach we refer the reader to reference [42].

In the rare-earth 4f quantum impurity problem we include all fourteen 4f orbitals, which form two manifolds—$j = 5/2$ and $j = 7/2$—split by the spin–orbit coupling; additional smaller splittings within each manifold arise due to the crystal field. We employ the fully-localized-limit double-counting correction in the atomic limit [49], i.e.

$$\Sigma_{DC} = U(N - 0.5) - J(0.5N - 0.5)$$

with the corresponding Ln$^{+}$ nominal atomic occupancies $N$. The chosen double-counting correction is orbitally-independent since a perturbative use of the mBJ potential does not induce a significant change in the 4f level splitting compared to LDA. All calculations are carried out for a temperature of 290 K.

2.2. Ab initio calculation of the screened Coulomb interaction $U$

The Coulomb repulsion on an $f$ shell is determined by four Slater parameters $F^0, F^2, F^3$ and $F^5$. In strongly localized Ln 4f shells, the parameters $F^2, F^3$ and $F^5$ are well known to exhibit virtually no material dependence. Furthermore, we use the standard approximation fixing the ratios of $F^0/F^2$ and $F^0/F^3$ to 451/675 and 1001/2025 obtained for a hydrogen-like 4f wavefunction [50]. The actual measured values $F^2, F^3$ and $F^5$ extracted from optical measurements along the RF$_3$ series are in good agreement with this approximation [51]. With this approximation, $F^2, F^3$ and $F^5$ are given by a single parameter—the Hund’s rule coupling $J_H$—for which we employ the values from reference [51]. The parameter $F^0 \equiv U$, in contrast, is strongly reduced from its atomic value by screening processes in solids; this screening is determined by the electronic structure of a given compound.

In order to calculate $U$ for the LnN series, we developed a constrained DFT + Hubbard-I (cDFT + Hubbard-I) technique based on the well-known constrained-DFT (cDFT) method for calculating the screened Coulomb interaction. In standard cDFT [52–56], the target shell occupancy (e.g. 4f) on a chosen site is constrained to a predefined value with the rest of the electrons allowed to screen it. By increasing or
decreasing this constrained occupancy one can evaluate the cost in interaction energy of placing electrons on the target shell, i.e. the parameter $U$. Its value is extracted either from the change in total energy due to the variation in occupancy or from the corresponding energy shift of the target band. The cDFT method is not free of uncertainties, related to separating out the kinetic and interaction energy contributions to the total energy cost [55, 56] as well as to the inter-site interaction between constrained shells. To reduce the impact of the latter, cDFT calculations are typically carried out for reasonably large supercells so that constrained sites are well separated in the real space.

For rare-earth semiconductors, the applicability of standard cDFT is questionable. The only metallic bands in their DFT electronic structure are of Ln 4f character (in contrast to the case of Ln metals, where 6s and 5d metallic bands are also present and thus cDFT performs reasonably well [55]). In cDFT, the constrained charge on a chosen Ln site will thus be screened by metallic 4f states. However, the metallic 4f bands with their contribution to screening are an artifact of DFT, since in reality the 4f electrons on Ln ions are essentially quasiatomic. A related problem is that the pd semiconducting bands in DFT are strongly impacted by hybridization with the 4f metallic band in the middle of the pd gap, with the gap magnitude enhanced to about 2.5 eV. The DFT band structure for the LnN series is thus far from being realistic.

In our cDFT + Hubbard-I approach, we instead exploit the natural ability of the Hubbard-I approximation to constrain the 4f shell occupancy to chosen integer values while keeping the shell localized. The DMFT impurity problem within this approximation is reduced to diagonalization of the 4f Hamiltonian [57]: 

$$\hat{H}_\text{int} = \hat{H}_{\text{tdd}} + \hat{H}_U = \sum_{\Lambda \Lambda'} \epsilon_{\Lambda \Lambda'} f^\dagger_{\Lambda \Lambda'} f_{\Lambda \Lambda'} + \hat{H}_U, \quad (1)$$

where $f_{\Lambda \Lambda'}$ $(f^\dagger_{\Lambda \Lambda'})$ is the creation (annihilation) operator for the Ln 4f orbital labeled by the combined spin–orbital index $\Lambda = m\sigma$ (with $m$ and $\sigma$ being the magnetic and spin quantum numbers, respectively), $\hat{H}_U$ is the on-site Coulomb repulsion. The one-electron level-position matrix $\hat{\epsilon}$ reads:

$$\hat{\epsilon} = -\mu + \hat{H}^\mu_{KS} - V, \quad (2)$$

where $\mu$ is the chemical potential, $\hat{H}^\mu_{KS} = \sum_{k \in \text{BZ}} \hat{P}_k \hat{H}_{\text{KS}} \hat{P}_k^\dagger$ is the KS Hamiltonian projected to the basis of 4f Wannier orbitals and summed over the Brillouin zone, $\hat{P}_k$ is the corresponding projector between the KS and Wannier spaces [44]. The shift $V$ in the standard DFT + Hubbard-I should be equal to the double counting correction term $\Sigma_{\text{DC}}$ as can be shown by a high-frequency expansion of the DMFT bath Green’s function [49].

In the cDFT + Hubbard-I approach we instead treat $V$ as a uniform potential applied to the 4f shell on a given site and choose its value to constrain the occupancy. In practice, we perform cDFT + Hubbard-I calculations with a trial value $U_{\text{GH}}$ for the Coulomb interaction parameter and compute

$$V_i = U_{\text{GH}}(N_i - 1/2) - J_{\text{H}}(N_i^2/2 - 1/2),$$

which is the target 4f occupancy at the Ln site $i$. We fix $N_i$ to $N_{\text{GS}} + 1$ and $N_{\text{GS}} - 1$, respectively, on two chosen Ln sites in a large supercell, where $N_{\text{GS}}$ is the ground-state 4f occupancy for a given Ln ion. On all other Ln sites $N_i^2$ equals $N_{\text{GS}}$. For a reasonably large value of $U_{\text{GH}}$ one obtains, with this choice for $V_i$, the required occupancies $N_i^2$ in DFT + Hubbard-I.

In order to understand why the described procedure for fixing the 4f occupancy works, let us recall the behavior of this occupancy vs $V$ in DFT + Hubbard-I. As a function of $V$, the ground-state occupancy $N_{\text{GS}}$ forms an upward staircase with each plateau corresponding to an integer value $N_{\text{GS}}$ between 0 and 14. The width of each plateau is about $U_{\text{GH}}$. The transitions between the plateaus, which are step-like in the purely atomic case, are somewhat smoothed by hybridization effects. One may notice that in a purely atomic case with $J_{\text{H}} = 0$ and $H^\mu_{KS} = 0$, the choice $V = U_{\text{GH}}(N_i - 1/2)$ corresponds to the middle of the plateau for the occupancy $N_i$. Of course, in a realistic case this will not exactly be the case. However, for a reasonably large $U_{\text{GH}}$ one may still expect to obtain the ground-state occupancy $N_i$ with this value of $V$. Alternatively, one could explicitly evaluate the dependence of $N_{\text{GS}}$ vs $V$ for each Ln site at each iteration to obtain a set of optimal $\{V_i\}$ values to fix the target occupancies. We did not need this more complex procedure, since the simple guess for $V$ described above was found to be sufficient to fix the required $N_i$ for all the mononitrides under consideration. The value of $U_{\text{GH}}$ in cDFT + Hubbard-I calculations can be chosen quite arbitrarily, though, as explained above, it needs to be sufficiently large to have well defined plateaus for integer 4f occupancies as a function of $V$. We fixed it at 10 eV.

Once the cDFT + Hubbard-I calculations converge, the value of $U$ can be extracted from the difference of averaged $ff$ blocks of the KS Hamiltonian $\langle \hat{H}_{\text{KS}}^f \rangle$ between the two sites with constrained occupancies. Namely, the orbital/spin average of $\langle \hat{H}_{\text{KS}}^f \rangle = \frac{1}{2}\sum_{\Lambda} \langle \hat{H}_{\text{KS}}^f \rangle_{\Lambda \Lambda}$ for a given occupancy $N$ reads

$$\langle \hat{H}_{\text{KS}}^f \rangle_N = \langle \hat{H}_{\text{KS}}^f \rangle + U(N - 1/2) - J_{\text{H}}(N/2 - 1/2), \quad (3)$$
where \( \langle H^f_{\text{KS}} \rangle \) is this average excluding the contribution of the intra-shell Coulomb repulsion, for the latter we assume the fully-localized limit form as given by the second and third terms on the right-hand side. Since \( \langle H^f_{\text{KS}} \rangle \) does not depend on the 4f shell occupancy, one finds:

\[
U = \frac{1}{2} \left[ \langle H^f_{\text{KS}} \rangle_{N+1} - \langle H^f_{\text{KS}} \rangle_{N-1} + J_1 \right],
\]

which is the equation we used to extract \( U \) from our cDFT + Hubbard-I results. We stress that the KS 4f band position given by equation (3) exhibits virtually no dependence on \( U_{\text{cHI}} \). It depends only on the effective value of \( U \) that describes the interaction between localized electrons in LDA inducing the corresponding shift of the KS band position. This is the value that we wish to extract by our method. \( \langle H^f_{\text{KS}} \rangle_N \) is the average position of the KS 4f level when its occupancy is constrained to \( N \). This KS level position depends only on the DFT + Hubbard-I charge density, which is expected to be rather insensitive to \( U_{\text{cHI}} \) once the 4f shell becomes localized at a given occupancy. Some very weak influence of \( U_{\text{cHI}} \) on the resulting \( U \) cannot be excluded, since larger \( U_{\text{cHI}} \) should result in somewhat more localized 4f states impacting the resulting charge density and, correspondingly, the KS 4f level position. But this effect is likely very small, and in practice we observe virtually no dependence of our final \( U \) on the choice of \( U_{\text{cHI}} \).

The present technique thus evaluates \( U \) for a realistic electronic structure of the Ln semiconductors, in which the 4f states are localized by the Hubbard interaction and do not contribute to any metallic screening of the constrained charge.

We also note that the average \( \langle H^f_{\text{KS}} \rangle_N \) is not equal to the centreweight of the corresponding 4f band. The latter is impacted by hybridization effects, leading to the complex problem of removing these (kinetic energy) effects from the cDFT estimation for \( U \) [56]. In contrast, \( \langle H^f_{\text{KS}} \rangle_N \) gives the 4f level position once hybridization of 4f with other states, within the energy window, is suppressed. Since in our calculations we employ a large window including all relevant valence bands, our estimation for \( U \) is essentially free from any admixture of hybridization effects.

Our cDFT calculations were carried out for a 32 atoms supercell with 15 \( k \)-points in the irreducible Brillouin zone. Consistently with the mBJ + Hubbard-I calculations for LnN, the energy window for the Wannier projection was chosen to be \([-9.5 \div 13.6] \) eV around the Fermi level.

### 3. Results and discussion

All rare-earth mononitrides \( \text{LnN} \) crystallize in the simple fcc rocksalt structure with decreasing lattice constant along the series. In our calculations, we have employed experimental lattice constants as summarized in reference [3]. We have performed calculations for eight members of the \( \text{LnN} \) series with \( \text{Ln} = \) Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er.

#### 3.1. Coulomb interaction \( U \) along the \( \text{LnN} \) series

We first present the evolution of the Coulomb interaction parameter \( U \) along the \( \text{Ln} \) mononitride series, as obtained by the cDFT + Hubbard-I method. The value of \( U \) increases along the series from 6.87 eV for PrN to 8.91 eV for ErN (figure 1(a) and table 1). This effect is caused by the corresponding enhancement in the 4f shell localization manifested in the well-known reduction of the \( \text{Ln}^{3+} \) ionic radius along the lanthanide series. \( U \) exhibits a quasi-linear trend as a function of the 4f shell occupancy \( \eta_f \), with a slightly more rapid increase in the beginning of the series, from Pr to Nd.

Previously, the \( U \) values along this series have been estimated by Larson \textit{et al} [23], who first computed the bare unscreened value of \( F^0 \) for \( \text{Ln}^{3+} \) ions and then applied a constant factor to simulate its reduction by screening in \( \text{LnN} \) compounds. The screening factor was extracted in reference [23] by comparing the bare Gd \( F^0 \) with the value of \( U \) needed to align the 4f band position in GdN calculated by LSDA + \( U \) with that measured in photoemission. Their resulting \( U \) values are about 10% larger than ours (e.g., for GdN \( U = 9.2 \) eV as compared to our value of 8.13 eV) and exhibit a somewhat more pronounced and non-monotonic increase along the series.

The Hund’s coupling \( J_{11} \), listed in the second row of table 1, is also progressively growing along the series, with values reaching from \( J_{11} = 0.73 \) eV in PrN to \( J_{11} = 1.05 \) eV in ErN. As noted above, \( J_{11} \) for the 4f shell is barely affected by the crystalline environment, the reported values for \( J_{11} \) were extracted from optical measurements of \( F^2, F^3 \) and \( F^5 \) in rare-earth metals [51].

#### 3.2. Trends in the \( \text{LnN} \) electronic structure

The calculated \( \text{LnN} \) \( k \)-integrated spectral functions are shown in figure 2 together with available experimental x-ray photoemission (XPS), x-ray emission (XES) and x-ray absorption (XAS) spectra. As
Figure 1. (a) Screened on-site Coulomb interaction $U$ along the $LnN$ series, calculated from cDFT + Hubbard-I (red lines–points). Further shown are values for $U$ reported in reference [23], which were obtained by Hartree–Fock calculations and scaled to fit photoemission data for GdN. (b) Optical gap (red lines–points) and band gap (blue lines–points), calculated from mBJ + Hubbard-I. For heavier rare-earths starting with $Ln$ = Gd, the band gap becomes indirect and is slightly smaller than the direct optical gap at $X$. For comparison, experimental values for the optical gap are shown (red symbols), adapted from references. (a) [17], (b) [4], (c) [9], (d) [10], (e) [1], (f) [5], and (g) [58].

Table 1. Computed values of the screened Coulomb interaction $U$ and optical gaps in the rare-earth mononitriles. Tabulated are further the experimental values of the Hund’s coupling $J$, employed in our calculations and extracted from reference [51] (for rare-earth metals). For comparison, experimental data of optical gaps are listed, taken from several studies performed during the last 20 years.

<table>
<thead>
<tr>
<th>$Ln$</th>
<th>$U$ (eV)</th>
<th>$J_H$ (eV)</th>
<th>Optical gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrN</td>
<td>6.87</td>
<td>0.73</td>
<td>1.02</td>
</tr>
<tr>
<td>NdN</td>
<td>7.23</td>
<td>0.77</td>
<td>1.26</td>
</tr>
<tr>
<td>SmN</td>
<td>7.63</td>
<td>0.85</td>
<td>1.47</td>
</tr>
<tr>
<td>GdN</td>
<td>8.13</td>
<td>0.92</td>
<td>1.72</td>
</tr>
<tr>
<td>TbN</td>
<td>8.33</td>
<td>0.95</td>
<td>1.70</td>
</tr>
<tr>
<td>DyN</td>
<td>8.52</td>
<td>0.98</td>
<td>1.81</td>
</tr>
<tr>
<td>HoN</td>
<td>8.67</td>
<td>1.01</td>
<td>2.02</td>
</tr>
<tr>
<td>ErN</td>
<td>8.91</td>
<td>1.05</td>
<td>2.14</td>
</tr>
</tbody>
</table>

expected, the topmost valence bands are mainly of N 2$p$ character and the conduction bands of $Ln 5d$ character. Our calculations predict a semiconducting electronic structure for all $LnN$, with valence N 2$p$ and conduction $Ln 5d$ bands never overlapping in energy. The $Ln 4f$ states are split into an occupied lower Hubbard band (LHB) and unoccupied UHB. The occupied 4$f$ states progressively shift to lower energies along the series, from PrN to ErN; this evolution is due to the well-known increase of the 4$f$ binding energy along the rare-earth series. The Hubbard bands further split into multiple peaks due to transitions between quasiatomic multiplets. This multiplet splitting is a characteristic feature of $Ln 4f$ states weakly hybridizing with the N 2$p$ and $Ln 5d$ states and thus keeping a quasi-atomic character in solids. The multiplet splitting is characteristic for each $Ln$ element and is absent in the half-filled Gd 4$f$ shell which displays two sharp Hubbard bands at $-7$ and $+7$ eV, respectively. The position of the GdN LHB agrees well with the experimental XPS spectrum of reference [59]. The 4$f$ UHB is about 14 eV above the LHB, in agreement with the magnitude of effective $U_{eff} = U + 6J_H$ for a half-filled $f$ shell.

Another, smaller peak around $-2$ eV is clearly visible in the GdN XPS spectrum and is identified by our calculations as the N 2$p$ band. The N 2$p$ states are further resolved in N K-edge XES data, while the unoccupied $Ln 5d$ states are probed by XAS. They both well match our calculated spectrum, thus validating our methodology in the case of Gd mononitride. GdN is by far the most investigated compound of the $LnN$ series, both experimentally and especially theoretically, since its electronic structure can—due to its
Figure 2. Spectral functions of LnN (Ln 4f in red, N 2p in blue, Ln 5d in green). For comparison, available experimental XPS (solid black lines), XES (blue lines) and XAS (green lines) spectra are shown. Experimental spectra in arbitrary units reproduced from (a) reference [18], (b) reference [59], (c) reference [60] and (d) reference [58].

half-filled 4f shell and the absence of multiplet effects—be qualitatively captured without employing DMFT. Hence, we will in the following rather concentrate on other, less explored compounds.

Unfortunately, there are few experimental spectra available for the rest of the LnN series. For the existing ones, i.e. an XPS spectrum for HoN [58] as well as XES and XAS spectra for SmN [18], DyN [18] and HoN [58], our ab initio electronic spectra agree very well with experiment, as can be seen in figure 2. In particular, a valence-band XPS is available only for HoN; as one sees, the position of the occupied 4f band and its splitting into two well separated manifolds is very well reproduced by our calculations.

In figure 1(b) we display our calculated values for the optical gap along the LnN series, see also table 1. These values are extracted from the LnN k-resolved spectral functions (some of them are shown in figures 3 and 4). Despite their progressive downward shift and changing shape along the series, the Ln 4f states never touch the bottom of the conduction band or the top of valence band. Therefore, for all investigated compounds the direct optical gap at X is formed between the N 2p and the Ln 5d states. The optical gap progressively increases from 1.02 eV in PrN to 2.14 eV in ErN. A comparison to available experimental data (figure 1(b) and table 1) reveals a qualitatively similar, though less pronounced trend in experiment. Our
calculations predict an overall steady increase of the optical gap along the series, with two noticeable peculiarities, i.e. a kink from Pr to Nd and a plateau between Gd and Dy. A similar non-trivial gap evolution vs $n_f$ is observed in experiment, with the value of the optical gap even slightly decreasing from Gd to Dy. The gaps’ absolute value is slightly overestimated by our mBJ + Hubbard-I methodology. For example, in the experimentally well investigated compound GdN, the difference between theoretically predicted and experimentally measured gap size is around 0.3 eV. Such a systematic overestimation seems to be a general feature of the mBJ potential applied to $d$-electron conduction states, as previously observed in the case of $d^0$ titanates [48].

Interestingly, our calculations predict the band gap to become indirect in the second half of the series due to the maximum of the valence band shifting from the X to $\Gamma$ point (cf figures 3 and 4). Such a shift is absent in the pure DFT band structure, though the N 2p band maximum at X becomes more shallow for heavy Ln, see appendix figure 5. With the localized 4f nature properly included in DFT + Hubbard-I, the pd gap drastically shrinks once the metallic 4f bands are removed by the on-site Coulomb interaction. This gap reduction results in a stronger downward shift of the 2p band maximum at X by pd hybridization. The hybridization shift at X grows along the series due to the reducing cell volume with the corresponding increase in pd hopping. This results in the band gap becoming indirect $\Gamma - X$ starting from GdN.

This trend was previously only roughly captured by LSDA + $U$ calculations of Larson et al [23]. In the case of completely empty (LaN) and filled (LuN) 4f bands they obtained direct and indirect band gaps, respectively. However, for all considered compounds with a fractional 4f occupancy, from PrN to YbN, an indirect gap was predicted for the paramagnetic phase. Therefore, a sharp transition to an indirect gap was predicted once the 4f band becomes partially occupied; the calculated band gap exhibits no clear trend along the series from Pr to Yb. Our calculations directly treating the paramagnetic phase rather predict a smooth evolution of the pd gap along the series.
We will now supplement the general picture presented above with a more detailed discussion of four selected compounds—NdN, SmN, TbN, and HoN—that exemplify the electronic structure evolution along the LnN series.

3.3. NdN

In figure 3(a) we show the computed k-resolved spectral function of NdN in the vicinity of the Fermi energy, i.e. from −6 to 6 eV, while the overall k-summed spectral function in a larger energy range has been presented in figure 2(b). Like in all investigated LnN, we obtain a Ln$^{3+}$ configuration, resulting in three electrons in the Nd 4f shell. As clearly visible from the k-integrated spectral function in figure 2(b), the Nd 4f states form a rather sharp LHB centered around −4 eV, while the unoccupied UHB spreads from 3 to almost 10 eV due to the effect of multiplet splittings. The band gap of 1.26 eV is direct and located at the X point, as one sees from the NdN k-resolved spectral function (figure 3(a)). The calculated gap magnitude, 1.26 eV, is slightly overestimated by our calculations, since optical measurements in references [4, 17] reported 0.9–1.0 eV. This is consistent with the systematic overestimation of pd gaps by the mBJ potential, as noted above. In spite of this overestimation, our theoretical value of the NdN band gap still agrees with experiment significantly better than previous calculations. LSDA + U calculations in reference [23] reported an (indirect, majority-spin) gap of only 0.3 eV in NdN, while earlier calculations predicted a half-metallic state [22]. According to our calculations, paramagnetic NdN is clearly a pd semiconductor, in agreement with transport measurements [17]. The unoccupied 4f states are located approximately 2 eV above the conduction band minimum. They weakly hybridize with the conduction band, but do not form the conduction band minimum, as suspected recently in reference [4]. We note, however, that our theoretical predictions are not at odds with the measurement of the optical conductivity in reference [4]. An earlier onset of the conductivity in NdN of around 0.2 eV compared to GdN, can be explained not only by the presence of additional states, i.e. the rare-earth 4f states, at the bottom of the conduction band, but also by an increase of the pd gap along the LnN series, as predicted by our calculations.

3.4. SmN

Resistivity measurements clearly indicate a semiconducting nature for SmN [18], in the paramagnetic as well as in the magnetically ordered state below 20–27 K [2, 18]. However, previous studies within LSDA + U [18, 23, 24] predicted a zero gap and varying position of the Sm 4f states depending on the choice of U. Our calculated k-integrated spectral function of SmN is presented in figure 2(c), while a zoom into the k-resolved spectrum around the Fermi energy is provided in figure 3(b). Due to an increase in the 4f binding energy, the occupied 4f states in SmN lie lower in energy compared to NdN. They are located in the...
range from $-8$ to $-4$ eV and split into several sharp peaks by multiplet effects figure 2(c). The unoccupied UHB extends between $2.5$–$10$ eV, above the valence band maximum. For SmN, there are N K-edge x-ray emission (XES) and absorption (XAS) spectra available in reference [18], which probe the occupied N 2p and Sm 5d states, respectively. They are shown in figure 2(c). Overall, the shape of experimental and theoretical spectra agrees well, though the energy axis position of the XES and XAS spectra, which cannot reliably be probed in experiment, has been adjusted to match our theoretical spectrum. Unfortunately, an x-ray photoemission spectrum (XPS), which would probe the total occupied spectrum including the rare-earth 4f states, is not yet available for SmN.

The k-integrated spectral function in figure 2(c) could give the impression that the Sm 4f states form the conduction band minimum. However, this is not the case, as can be seen from the k-resolved spectrum in figure 3(b). The lowest-lying unoccupied 4f states hybridize with the Sm 5d states and are closer to the conduction minimum at X than in NdN, but still around 1 eV higher in energy. The direct band gap in SmN is again formed between the occupied N 2p and the unoccupied Sm 5d bands. This picture is at odds with the conclusion of reference [9], who attributed a broad absorption feature centered around 0.5 eV in the optical conductivity of SmN to the presence of Sm 4f states in the semiconducting gap. However, this additional broad absorption feature is more likely an effect of nitrogen vacancies, which are known to induce in-gap states. The latter hypothesis was followed in reference [11] and has been carefully studied by the authors of reference [9] later on for a very similar absorption feature in DyN [5]. According to precise measurements of the optical gap in SmN [9, 10], our theoretically predicted gap of 1.47 eV seems to be overestimated by around 0.2 eV.

### 3.5. TbN

Let us now turn to a rare-earth mononitride with a more than half-filled 4f shell. Tb$^{3+}$ has eight electrons in the 4f shell, i.e. one electron more compared to the half-filled case. The occupied 4f states in TbN are split into a manifold between $-10$ and $-5$ eV, exhibiting further intrinsic multiplet splittings, and a single peak slightly above $-2$ eV located within the N 2p band and weakly hybridizing with it (figure 2(e)). The peak above $-2$ eV is associated with the transition by electron removal to the half-filled Hund’s rule $^8S_{5/2}$ state. The low-lying 4f manifold is due to excited states of the half-filled shell, which have much higher energy than the Hund’s rule state.

A density of states for TbN was previously calculated by Aetts et al [22] by a SIC LSDA approach. This study predicted occupied 4f states below $-13$ eV and unoccupied ones right above the Fermi energy, which does not seem to be plausible. An LSDA + U band structure for TbN was calculated by Larson et al [23]. They found two competing solutions, one dominated by the material’s crystal fields while the second one induced by atomic Hund’s rules. In our many-body mBJ + Hubbard-I approach we do not encounter this ambiguity since it includes the local Coulomb interaction on the 4f shell and weakly hybridizing with it (figure 2(e)). The peak above $-2$ eV is associated with the transition by electron removal to the half-filled Hund’s rule $^8S_{5/2}$ state. The low-lying 4f manifold is due to excited states of the half-filled shell, which have much higher energy than the Hund’s rule state.

A density of states for TbN was previously calculated by Aetts et al [22] by a SIC LSDA approach. This study predicted occupied 4f states below $-13$ eV and unoccupied ones right above the Fermi energy, which does not seem to be plausible. An LSDA + U band structure for TbN was calculated by Larson et al [23]. They found two competing solutions, one dominated by the material’s crystal fields while the second one induced by atomic Hund’s rules. In our many-body mBJ + Hubbard-I approach we do not encounter this ambiguity since it includes the local Coulomb interaction on the 4f shell and weakly hybridizing with it (figure 2(e)). The peak above $-2$ eV is associated with the transition by electron removal to the half-filled Hund’s rule $^8S_{5/2}$ state. The low-lying 4f manifold is due to excited states of the half-filled shell, which have much higher energy than the Hund’s rule state.

A density of states for TbN was previously calculated by Aetts et al [22] by a SIC LSDA approach. This study predicted occupied 4f states below $-13$ eV and unoccupied ones right above the Fermi energy, which does not seem to be plausible. An LSDA + U band structure for TbN was calculated by Larson et al [23]. They found two competing solutions, one dominated by the material’s crystal fields while the second one induced by atomic Hund’s rules. In our many-body mBJ + Hubbard-I approach we do not encounter this ambiguity since it includes the local Coulomb interaction on the 4f shell and weakly hybridizing with it (figure 2(e)). The peak above $-2$ eV is associated with the transition by electron removal to the half-filled Hund’s rule $^8S_{5/2}$ state. The low-lying 4f manifold is due to excited states of the half-filled shell, which have much higher energy than the Hund’s rule state.

### 3.6. HoN

The Ho$^{3+}$ 4f shell hosts ten electrons. Like almost all LnN, HoN exhibits ferromagnetic order below its Curie temperature of $T_C = 18$ K [61], while above it is paramagnetic. The k-integrated spectral function of HoN is shown in figure 2(g).

Due to multiplet effects, the occupied 4f states are split into two main manifolds centered around $-7$ and $-4.5$ eV, respectively. The UHB, instead, spreads from 4.5 to 8 eV. The two main manifolds of the LHB are clearly visible in the experimental x-ray photoemission (XPS) spectrum of reference [58], which we have reproduced in figure 2(g). The overlay with our theoretical spectrum shows an excellent agreement. The shoulder at the low binding energy side of the XPS spectrum matches the position and shape of the N 2p states. The N 2p states were further probed by N K-edge x-ray emission (XES) in reference [58]. The experimental XES spectrum shows rather broad N 2p states with a low-energy tail extending to almost
−8 eV, which led the authors of reference [58] to the conclusion of strong \( p - f \) hybridization in HoN. In our calculations, the Ho 4f states are well localized and the \( p - f \) hybridization is not that pronounced. The long tails, as well as the spectral weight in the gap, observed in XES might thus more likely be the consequence of defects present in the samples. In the detailed experimental study of reference [58], additionally, the unoccupied \( Ln \) 5d states were probed in x-ray absorption (XAS). The corresponding XAS spectrum is reproduced in figure 2(g).

Our calculation predicts for HoN an optical gap of 2.02 eV at \( X \) (figure 4(b)). Again, the computed optical gap seems to be overestimated compared to its experimental value of 1.48 eV [58]. Similar to TbN, the band gap in HoN is indirect with the valence band maximum located at \( \Gamma \), and it is 0.2 eV smaller than the optical gap.

4. Conclusions

We have computed the paramagnetic electronic structure of eight rare-earth mononitrides \( LnN \) (with \( Ln = \) Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er) by employing an advanced first-principles mBJ + Hubbard-I approach. This approach combines a quasi-atomic treatment of electronic correlations in the \( Ln \) 4f shell with an improved description of semiconducting band gaps by the non-local mBJ exchange potential. The screened on-site Coulomb interaction in the 4f shells is evaluated from first principles by a novel cDFT + Hubbard-I methodology that we describe in detail in the present work. From the calculated spectral functions we obtained the evolution of the semiconducting band gap along the \( LnN \) series as well as position and multiplet spitting of the \( Ln \) 4f states. A semiconducting gap of \( pd \) type is predicted for all investigated compounds, with the gap magnitude ranging from 1.02 eV in PrN to 2.14 eV in ErN. The band gap is direct in light lanthanide \( LnN \) up to SmN; it becomes indirect \( \Gamma - X \) for heavy \( Ln \). The predicted evolution of the band gap magnitude along the series agrees qualitatively with available data from optical measurements; theoretical gap values are slightly systematically overestimated. The calculated \( k \)-integrated spectral functions agree well with available spectra from x-ray photoemission (XPS), x-ray emission (XES) and x-ray absorption (XAS) spectroscopy. The present work provides a compendium of computed spectral functions of the rare-earth mononitrides \( LnN \), which can be useful for future experimental and theoretical investigations.

Overall, the combination of the quasiatomic Hubbard-I treatment for local 4f correlation with the non-local mBJ exchange potential has shown promising predictive capabilities for a variety of rare-earth based semiconductors including the rare-earth mononitrides \( LnN \), rare-earth fluorosulfides \( LnSF \) [41] and rare-earth sesquioxides \( Ln_2O_3 \) [42].

Acknowledgments

We thank Silke Biermann and James Boust for fruitful discussions. This work was supported by the Austrian Science Fund (FWF): Schrödinger fellowship J-4267. We thank the computer team at CPHT for support.

Data availability statement

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

Appendix

Representatively, we show in figure 5 the paramagnetic KS band structure of NdN and TbN, computed by employing the mBJ potential. The partially filled \( Ln \) 4f bands are metallic and located within the gap between the \( N \) 2p and \( Ln \) 5d bands. Due to the presence of \( Ln \) 4f in-gap states, the \( pd \) gap is enhanced to around 3 eV. Along the \( LnN \) series, the occupied \( Ln \) 4f states are moving toward higher binding energies. Hence, in the KS band structure of NdN they are mainly hybridizing with the conduction \( Ln \) 5d bands, while in TbN the 4f bands mainly mix with the N 2p valence bands.

ORCID iDs

Anna Galler https://orcid.org/0000-0002-8596-7784
Leonid V Pourovskii https://orcid.org/0000-0003-4003-3539
References

[38] Hubbard J 1963 Proc. R. Soc. A 276 238