Self-consistent Hubbard parameters from density-functional perturbation theory in the ultrasoft and projector-augmented wave formulations

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The self-consistent evaluation of Hubbard parameters using linear-response theory is crucial for quantitatively predictive calculations based on Hubbard-corrected density-functional theory. Here, we extend a recently-introduced approach based on density-functional perturbation theory (DFPT) for the calculation of the on-site Hubbard $U$ to also compute the inter-site Hubbard $V$. DFPT allows to reduce significantly computational costs, improve numerical accuracy, and fully automate the calculation of the Hubbard parameters by recasting the linear response of a localized perturbation into an array of monochromatic perturbations that can be calculated in the primitive cell. In addition, here we generalize the entire formalism from norm-conserving to ultrasoft and projector-augmented wave formulations, and to metallic ground states. After benchmarking DFPT against the conventional real-space Hubbard linear response in a supercell, we demonstrate the effectiveness of the present extended Hubbard formulation in determining the equilibrium crystal structure of Li$_x$MnPO$_4$ ($x=0.1$) and the subtle energetics of Li intercalation.

I. INTRODUCTION

Exchange-correlation (xc) functionals based on the Hubbard extensions [1–3] to density-functional theory (DFT) [4, 5] have proven to be quite effective in describing complex systems, both solid-state and molecular (see e.g. Refs. [6–12]). As it is well-known from literature on DFT+$U$ and DFT with dynamical mean-field theory (DFT+DMFT) [13–17], a reliable and consistent method to evaluate the Hubbard parameters is key to achieve quantitative predictions. Although the empirical determination of these parameters is still common practice, different methods to compute their value from first principles have been introduced, including constrained DFT (cDFT) [18–26], Hartree-Fock based approaches [27–31], and the constrained random phase approximation (cRPA) [32–31]. A linear-response formulation of cDFT (LR-cDFT) was introduced in Ref. [32] and generalized to the calculation of the inter-site Hubbard parameters $V$ in Ref. [33] (see also Refs. [34, 35]). Recent work [36, 37] involving some of the present authors, has highlighted the quantitative accuracy of DFT+$U$+$V$ calculations [33] with both on-site $U$ and inter-site $V$ effective parameters (here, $V$ bridges the on-site Hubbard manifold with the surrounding ligand ions), when based on the self-consistent evaluation of the Hubbard parameters using linear-response theory.

LR-cDFT has recently been recast via density-functional perturbation theory (DFPT) [38], allowing to overcome several challenges of the supercell approach of Ref. [32]. In fact, by constructing the response of the system to a localized perturbation through a series of independent monochromatic perturbations to the primitive unit cell (rather than from finite-differences between calculations in supercells as in LR-cDFT), it improves significantly the computational efficiency, accuracy, user-friendliness, and automation [38], as also demonstrated by several recent applications [46, 47, 49–51]. Key to this is indeed the capability to express perturbation theory in reciprocal space [52, 53].

Encouraged by the significant improvement in flexibility and accuracy obtained with DFT+$U$+$V$ and spurred by the need to calculate Hubbard parameters efficiently and consistently, we present here a generalization of the DFPT implementation to compute also the inter-site Hubbard $V$ in a self-consistent fashion. In addition, we extend the formulation to metallic systems [i.e., with fractionally occupied Kohn-Sham (KS) states], to ultrasoft (US) pseudopotentials (PPs) [55] and to the projector-augmented wave (PAW) method [56, 57]. These extensions are particularly useful for systems where transferability is paramount, where magnetism arises, and where the presence of localized valence states (e.g., semicore states promoted to valence or atomic states of $d$ or $f$ kind in transition-metal and rare-earth compounds), which require the use of very high kinetic energy cut-offs in the plane-wave expansion.

As a test case, we perform DFT+$U$ and DFT+$U$+$V$ calculations with self-consistent first-principles Hubbard parameters $U$ and $V$ (determined using DFPT) to study the structural properties and energetics (voltages) of a prototypical Li-ion cathode material Li$_x$MnPO$_4$ ($x=0.1$). Notably, the inclusion of the inter-site Hubbard $V$ improves the agreement of computed lattice parameters and voltages compared to the experimental values, as opposed to the case when only $U$ is taken into account.
The paper is organized as follows. Section II summarizes the formulation of DFT+$U+V$ [43]; Sec. III illustrates the linear-response approach to the calculation of Hubbard parameters $U$ and $V$, starting from a real-space formulation [42] (Sec. III A), reviewing its recent reciprocal-space implementation based on DFPT (Sec. III B), and adapting the latter to US and PAW formulations (Sec. III C); this is the main methodological advancement of the present paper. Section IV details a real-space formulation [42] (Sec. III A), reviewing its linear-response approach to the calculation of Hubbard parameters $U$ and $V$ obtained using DFT+$U$ and DFT+$U+V$. Finally, Sec. V presents our calculations, and Sec. VI after benchmarking the protocol designed to calculate the Hubbard parameters in Refs. [45] and [46], and then discuss its generalization to the case of US PPs and the PAW method. This section we briefly review the formulation of the extended Hubbard model in-
within each atom), or from the orthogonalized atomic orbitals (which are obtained by orthogonalizing the atomic orbitals from different sites) [61], or using (maximally localized) Wannier functions [62].

For the purpose of this work it is important to study the contribution to the KS potential stemming from the extended Hubbard correction. The action of this term on a KS pseudo-wavefunction can be easily obtained by taking the functional derivative of \( E_{\text{DFT}+U} \) with respect to the complex conjugate of the same pseudo-wavefunction [63]. The term corresponding to this functional derivative of \( E_{\text{U}+V} \) [see Eq. (2)] is:

\[
\hat{V}_{\text{Hub},\sigma}^\gamma = \sum_I \sum_{m_1 m_2} U^I \left( \frac{\delta_{m_1 m_2}}{2} - n^{I \sigma}_{m_1 m_2} \right) \hat{p}_{m_1 m_2}^I \\
- \sum_I \sum_{\sigma \neq \sigma'} \sum_{m_1 m_2} V^{IJ I' J'} \hat{p}_{m_1 m_2}^{I J} \hat{p}_{m_1 m_2}^{I' J'} . \tag{7}
\]

In the following, we present the DFT+\( U + V \) formalism for the case of US PPs and the PAW method. While many works are based on the projection of KS states on projector functions in the augmentation spheres (see Eq. (6) of Ref. [55]), this work uses projections on orthogonalized atomic orbitals, which are not restricted to the augmentation spheres. The main modifications that various terms undergo when US PPs or the PAW method is used relate to the fact that KS pseudo-wavefunctions are made “soft” by smoothing their profiles in the core regions so that it becomes necessary to augment the sum of their squares with the missing core-localized “hard” regions so that it becomes necessary to augment the sum of their squares with the missing core-localized “hard” parts in order to calculate the proper charge density [64]:

\[
rho_\sigma^\gamma(\mathbf{r}) = \sum_{\mathbf{k}} \sum_v \hat{\theta}_{\mathbf{F}, \mathbf{k} \sigma} |\psi_{\mathbf{k} \sigma}^\gamma(\mathbf{r})|^2 \\
+ \sum_{\mathbf{k}} \sum_v \hat{\theta}_{\mathbf{F}, \mathbf{k} \sigma} \sum_{\mu \nu} Q_{\mu \nu}^{\gamma(I)}(\mathbf{r} - \mathbf{R}_I) \langle \psi_{\mathbf{k} \sigma}^\gamma | \beta_{\mu I}^I \rangle \langle \beta_{\nu I}^I | \psi_{\mathbf{k} \sigma}^\gamma \rangle . \tag{8}
\]

As evident from this equation, the augmentation of the charge density is realized by adding localized augmentation charge densities \( Q_{\mu \nu}^{\gamma(I)}(\mathbf{r} - \mathbf{R}_I) \) that pertinent to the pseudopotential of the \( I^{th} \) atom, of type \( \gamma(I) \) at position \( \mathbf{R}_I \) through a projection of Kohn-Sham states on appropriately constructed localized functions \( \beta_{\mu I}^I(\mathbf{r}) \equiv \beta_{\mu}^{\gamma(I)}(\mathbf{r} - \mathbf{R}_I) \) that vanish at and beyond an atom-specific core radius [55] and that are labeled by atomic-state indices \( \mu \) and \( \nu \). Being deprived of the hard part around the nuclei, the soft KS states must satisfy a generalized orthonormality condition:

\[
\langle \psi_{\mathbf{k} \sigma}^\gamma | \hat{S} | \psi_{\mathbf{k'} \sigma'}^\gamma \rangle = \delta_{\sigma \sigma'} \delta_{\mathbf{k} \mathbf{k'}} , \tag{9}
\]

where \( \hat{S} \) is an overlap operator

\[
\hat{S} = 1 + \sum_{\mu \nu} \bar{q}_{\mu \nu}^{\gamma(I)} |\beta_{\mu I}^I\rangle \langle \beta_{\nu I}^I | , \tag{10}
\]

based on the same \( \beta \) functions of Eq. (8) and on augmentation charges defined as:

\[
q_{\mu \nu}^{\gamma(I)} = \int V_{\mu \nu}^{\gamma(I)}(\mathbf{r}) \, d\mathbf{r} , \tag{11}
\]

with \( V \) being the volume of the crystal. As a consequence, the soft KS states are calculated by solving the generalized KS equations [55, 65]:

\[
\hat{H}_{\sigma}^\circ |\psi_{\mathbf{k} \sigma}^\circ\rangle = \varepsilon_{\mathbf{k} \sigma}^\circ \hat{S} |\psi_{\mathbf{k} \sigma}^\circ\rangle , \tag{12}
\]

where \( \varepsilon_{\mathbf{k} \sigma}^\circ \) are the KS energies, and

\[
\hat{H}_{\sigma}^\circ = \hat{H}_{\text{DFT},\sigma}^\circ + \hat{V}_{\text{Hub},\sigma}^\circ , \tag{13}
\]

with \( \hat{H}_{\text{DFT},\sigma}^\circ \) being the DFT Hamiltonian (LSDA or spin-polarized GGA) and \( \hat{V}_{\text{Hub},\sigma}^\circ \) is the Hubbard potential given by Eq. (7). The overlap operator of Eq. (10) has to be used also as the kernel of all the scalar products between pseudo KS wavefunctions, as already exemplified in the generalized orthonormality condition, Eq. (9). The effective Hubbard corrective potential, Eq. (7), can thus be effectively obtained from the inclusion of the overlap operator in the expression of the projector on atomic states, Eq. (14):

\[
\hat{p}_{m_2 m_1}^{IJ} = \hat{S} |\varphi_{m_2}^\circ\rangle \langle \varphi_{m_1}^\circ | \hat{S} . \tag{14}
\]

This generalized expression of the projector is sufficient to obtain the atomic occupations as indicated in Eq. (5) using “soft” (atomic and KS) wavefunctions and, consequently, the generalization of the Hubbard energy, Eq. (2), and potential, Eq. (7), to implementations based on US PPs. The same generalized expression of the Hubbard functional obtained for US PPs can actually be used also for PAW, once augmentation quantities are properly adapted [57, 66] (see Sec. III C 2). This point is discussed in more detail in Appendix A.

III. CALCULATION OF HUBBARD PARAMETERS FROM LINEAR-RESPONSE THEORY

A. Definition of Hubbard parameters

The importance of the calculation of Hubbard parameters from first-principles using linear-response theory stems from the capability of the Hubbard corrections to remove the residual electronic self-interactions from approximate energy functionals, that manifests itself through an undesirable curvature of the total energy as a function of atomic occupations [32]. In fact, Hubbard effective interactions can be defined as the second derivatives of the total energy with respect to the total occupation of a given atom, i.e. with respect to the trace of the occupation matrix defined in Eq. (6) [12]:
with this definition, Hubbard corrections restore the desired piecewise linearity of the total energy. This can be achieved by perturbing the system with a shift in the potential acting on the Hubbard states of a given atom, \( \Delta V^J = \lambda^J \sum_m \hat{P}_{m1}^J \), and then computing the response of all the atomic occupations. Applying this to all the Hubbard atoms in the system allows to construct the bare and self-consistent susceptibility matrices (obtained, in practical calculations, respectively at the beginning of the perturbed run and at its self-consistent convergence):

\[
(\chi_0)_{IJ} = \frac{dn^I_{\sigma}}{d\lambda^J}, \quad (\chi)_{IJ} = \frac{dn^I}{d\lambda^J}.
\]

From these, the effective Hubbard parameters can be readily obtained [42]:

\[
U^I = (\chi^{-1} - \chi^{-1})_{II}, \quad V^{IJ} = (\chi^{-1} - \chi^{-1})_{IJ}.
\]

It is important to stress that the procedure outlined above is based on isolated perturbations; therefore, it requires the use of large supercells (whose size has to be increased until the convergence of \( U^I \) and \( V^{IJ} \)) that makes the computational cost and numerical noise rapidly increasing [42]. However, DFPT allows us to largely reduce these issues [48].

### B. DFPT with norm-conserving PPs: extension to \( V \) and to metallic systems

In order to overcome the difficulties alluded to in Sec. [III A] we have recently introduced an implementation of the LR approach outlined above using DFPT [48]. The scope of this section is to discuss the extension of this formalism to metallic systems and to the calculation of the inter-site interaction parameters \( V \). For the sake of simplicity, this discussion is based on a NC PPs implementation; the generalization to US PPs and the PAW method is discussed in Sec. [III C]. Within the framework of the DFPT implementation, the response of the KS wavefunctions to a small perturbation of the atomic potential [that induces a variation of the atomic occupations defined in Eq. [15]] is obtained as the solution of the perturbative problem resulting from a first-order variation of the KS equations:

\[
\left( \hat{H}_G - \varepsilon_{v\kappa\sigma} \right) \frac{d\psi_{v\kappa\sigma}}{d\lambda^J} = - \left( \frac{d\hat{V}_{\text{Hxc},\sigma}}{d\lambda^J} - \frac{d\varepsilon_{v\kappa\sigma}}{d\lambda^J} + \tilde{V}_{\text{pert}}^J \right) \psi_{v\kappa\sigma},
\]

where \( \tilde{V}_{\text{pert}}^J \) is the perturbing potential, \( \frac{d\hat{V}_{\text{Hxc},\sigma}}{d\lambda^J} \), \( \frac{d\varepsilon_{v\kappa\sigma}}{d\lambda^J} \), and \( \frac{d\varepsilon_{v\kappa\sigma}}{d\lambda^J} \) are the response Hartree and xc (Hxc) potentials, response KS wavefunctions, and response KS energies, respectively [48]. As detailed in Refs. [48, 54], the problem has to be solved self-consistently because the response of the KS eigenvalues and of the Hxc potential appearing on the right-hand side of Eq. [18] depend on the response of the KS wavefunctions, obtained from the solution of the perturbative problem in the equation above. Once convergence is achieved, the variation of the diagonal (with respect to atomic sites) atomic occupation matrices [that define the self-consistent susceptibility matrix in Eq. [13]] are obtained [47]:

\[
\frac{dn^I_{\sigma}}{d\lambda^J} = \sum_{k,v} \frac{\tilde{\delta}_{F,v\kappa\sigma}}{\eta^I} \left\langle \psi_{v\kappa\sigma} | \hat{p}_{m1}^J | \psi_{v\kappa\sigma} \right\rangle \frac{d\psi_{v\kappa\sigma}}{d\lambda^J} + \frac{d\varepsilon_{v\kappa\sigma}}{d\lambda^J} \left\langle \psi_{v\kappa\sigma} | \hat{p}_{m21}^J | \psi_{v\kappa\sigma} \right\rangle.
\]

The last term on the right-hand side of Eq. [19] comes from the derivative of the occupations of KS states appearing in Eq. [13] [58]:

\[
\frac{d\tilde{\delta}_{F,v\kappa\sigma}}{d\lambda^J} = \frac{1}{\eta} \delta \left( \frac{\varepsilon_{F} - \varepsilon_{v\kappa\sigma}}{\eta} \right) \left[ \frac{d\varepsilon_{F}}{d\lambda^J} - \frac{d\varepsilon_{v\kappa\sigma}}{d\lambda^J} \right],
\]

where \( \delta(\varepsilon) \equiv \frac{d\tilde{\delta}(\varepsilon)}{d\varepsilon} \) is a smooth approximation to the Dirac’s \( \delta \) function, \( \eta \) is a broadening parameter, \( \varepsilon_F \) and \( \frac{d\varepsilon_F}{d\lambda^J} \) are the Fermi energy and its shift (see Sec. II.C.4 of Ref. [54]). Obviously, the term \( \frac{d\tilde{\delta}_{F,v\kappa\sigma}}{d\lambda^J} \) is absent for semiconductors and insulators as their KS state occupations are either 0 or 1 and the smearing of the Fermi distribution function is irrelevant.

It is important to remark that, when LR calculations are based on the DFT+U+V ground state (for self-consistent evaluations of the Hubbard parameters [46, 54], the Hubbard correction enters the unperturbed Hamiltonian \( \hat{H}_G \) in Eq. [18], with the Hubbard potential given in Eq. [7]. However, as was pointed out in Ref. [48], the response of the Hubbard potential is not present in Eq. [18] so that the Hubbard parameters are obtained, consistently with their definition, as second derivatives of the DFT part only of the total energy.

The major advantage offered by the DFPT reformulation of LR-cDFT consists in the possibility to obtain the variation of atomic occupations as a sum of wavevector-specific contributions that can be computed independently from one another (thus leading to better scaling of the computational cost [48]) using the primitive cell of the system. In fact, the Fourier spectrum of a perturbation that has the periodicity of a supercell (as needed to eliminate the interactions with periodic replicas) only contains fundamental vectors of its reciprocal lattice that map into a corresponding \( \mathbf{q} \) points grid within the Brillouin zone corresponding to the primitive cell [48]. The total response of atomic occupations can thus be written
where the atomic site indices \( I \) and \( J \) have been decomposed as \( I = (l, s) \) and \( J = (l', s') \) indicating, respectively, the cell the atom belongs to \((l \text{ and } l')\) and its position within the cell \((s \text{ and } s')\). Here, \( N_q \) is the number of \( q \) points in the first BZ (note that the dimension of the \( q \) points grid reflects directly that of the supercell it is the reciprocal-space image of). \( \Delta q' \bar{n}_{m,1}^{s,\sigma} \) represents the lattice-periodic response (hence the over-bar) of the occupation matrix to a monochromatic perturbation with a lattice-periodic response (hence the over-bar) of the occupation matrix to a monochromatic perturbation with a wavevector \( \mathbf{q} \), and it can be linked to the lattice-periodic variations of the KS wavefunctions as follows [45]:

\[
\Delta q' \bar{n}_{m,1}^{s,\sigma} = \frac{1}{N_k} \sum_{l} N_h \sum_{\mathbf{k}} \sum_{l'} \sum_{\mathbf{k}'} \left\langle \hat{P}_{m,1}^{s',\sigma} \hat{P}_{m,2}^{s,\sigma} \bar{n}_{l,1}^{\sigma} \right\rangle \right.
\]

\[
\left. + \frac{1}{N_k} \sum_{l} N_h \sum_{\mathbf{k},1} \sum_{l'} \sum_{\mathbf{k}'} \left\langle \hat{P}_{m,1}^{s',\sigma} \hat{P}_{m,2}^{s,\sigma} \bar{n}_{l,1}^{\sigma} \right\rangle \right. \]

\[
\left. + \frac{\delta q,0}{N_k} \frac{1}{N_h} \sum_{\mathbf{k}} \sum_{l} N_h \sum_{\mathbf{k'}} \sum_{l'} \sum_{\mathbf{k}} \frac{1}{\eta} \frac{\Delta q' \varepsilon_F}{\eta} \Delta q' \varepsilon_F \right. \]

\[
\times \left\langle \bar{n}_{l,1}^{\sigma} \right\rangle \right. \left. \left\langle \hat{P}_{m,1}^{s',\sigma} \hat{P}_{m,2}^{s,\sigma} \bar{n}_{l,1}^{\sigma} \right\rangle \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \r...
susceptibility matrices using Eq. (15), from which the Hubbard interaction parameters are readily obtained as indicated in Eqs. (16) and (17).

C. Extension of DFPT to ultrasoft PPs and PAW

After reviewing the DFPT formalism for the calculation of the Hubbard parameters, we here specialize it to US PPs and the PAW method. We stress that only Hubbard-related terms will be discussed. The reader who is interested in a general discussion of DFPT with US PPs or PAW is encouraged to review the existing literature on the topic [58, 71].

1. Ultrasoft pseudopotentials

The Sternheimer equations that are solved in DFPT must be generalized to the US PPs case. After extensive but straightforward mathematical manipulations it can be shown that the final form of Eq. (21) in the US PPs case becomes:

\[
\left( \hat{H}_{k+q,\sigma}^o + \alpha \hat{O}_{k+q,\sigma} - \epsilon_{v,k\sigma} \hat{S}_{k+q} \right) \left| \Delta q' \bar{u}_{v,k\sigma} \right> = -\hat{P}_{v,k+q,\sigma} \left( \Delta q' \hat{V}_{\text{eff},k+q,k,\sigma} + \hat{V}_{\text{pert},k+q,k} \right) \left| \bar{u}_{v,k\sigma} \right>,
\]

where \( \hat{O}_{k+q,\sigma} \) and \( \hat{P}_{v,k+q,\sigma} \) are generalized as [72]

\[
\hat{O}_{k+q,\sigma} = \sum_{v'}^N \hat{S}_{k+q} \left| \bar{u}_{v,k+q,\sigma} \right> \left< \bar{u}_{v,k+q,\sigma} \right| \hat{S}_{k+q},
\]

\[
\hat{P}_{v,k+q,\sigma} = \theta_{F,v,k\sigma} - \sum_{v'}^N \gamma_{v,k\sigma, v'k+q\sigma} \times \hat{S}_{k+q} \left| \bar{u}_{v,k+q,\sigma} \right> \left< \bar{u}_{v,k+q,\sigma} \right|,
\]

In Eqs. (29)–(30), \( \hat{S}_{k+q} \) is the lattice-periodic part of the overlap operator \( \hat{S} \), which reads

\[
\hat{S}_{k+q} = 1 + \sum_{s,\mu,\nu} \gamma_{\mu,\nu}^{(s)} \left| \bar{\varphi}^s_{\mu,k+q} \right> \left< \bar{\varphi}^s_{\nu,k+q} \right|,
\]

and the orthonormality condition (9) now reads

\[
\left< \bar{u}_{v,k\sigma} \right| \hat{S}_{k+q} \left| \bar{u}_{v,k'\sigma} \right> = \delta_{v,v'} \delta_{\sigma,\sigma'},
\]

where the inner product is computed via integration over the volume of the primitive unit cell. In Eq. (29), the effective response potential \( \Delta q' \hat{V}_{\text{eff},k+q,k,\sigma} \) is defined as a sum of the standard Hxc response potential \( \Delta q' \hat{V}_{\text{Hxc},\sigma} \) [as in Eq. (24)], but which depends on the US PPs augmented response spin charge density [58] plus an extra US PPs specific term, namely:

\[
\Delta q' \hat{V}_{\text{eff},k+q,k,\sigma} = \Delta q' \hat{V}_{\text{Hxc},\sigma} + \sum_{s,\mu,\nu} \left< \bar{\varphi}^s_{\mu,k+q} \Delta q' \hat{V}_{\text{Hxc},\sigma} \right> \times \left| \bar{\varphi}^s_{\nu,k} \right> \left< \bar{\varphi}^s_{\nu,k} \right|.
\]

The quantities appearing in Eqs. (32) and (33) are defined in the Appendix B.

Various terms of the Hubbard correction undergo a similar generalization when US PPs are used. The Hubbard potential that is included in the unperturbed Hamiltonian \( \hat{H}_{k+q,\sigma} \) of Eq. (29), has the following expression:

\[
\hat{V}_{\text{Hubb},k+q,\sigma} = \sum_{s} \sum_{m_1 m_2} U^s \left( \delta_{m_1 m_2} - n_{m_1,\sigma} \right) \hat{P}_{s, m_1, m_2, k+q, k+q},
\]

\[
- \sum_{s} \sum_{s' (s' \neq s)} \sum_{R_s - R_{s'}} \sum_{m_1 m_2} V_{s's', s'\sigma} \hat{P}_{s, m_1, m_2, k+q, k+q} \times \hat{P}_{s', m_1, m_2, k+q, k+q},
\]

where

\[
n_{m_1,\sigma} = \frac{1}{N_k} \sum_k \theta_{F,v,k\sigma} \left< \bar{u}_{v,k\sigma} \right| \hat{P}_{s', m_1, m_2, k+q, k+q} \times \hat{P}_{s', m_1, m_2, k+q, k+q} \left| \bar{u}_{v,k\sigma} \right>.\]

In analogy with Eq. (30), the periodic, k-specific projector is generalized as follows:

\[
\hat{P}_{m_1, m_2, k, k} = e^{i k (R_l - R_{l'})} \hat{S}_{k} \left| \bar{\varphi}^{s}_{m_1, k} \right> \left< \bar{\varphi}^{s}_{m_1, k} \right| \hat{S}_{k},
\]

where the phase factor accounts for the possibility for the two atomic wavefunctions to belong to neighbor cells. In the first term of Eq. (34), \( n_{m_1 m_2} \) corresponds to \( n_{m_1 m_2} \), and \( \hat{P}_{m_1, m_2, k, k} \) corresponds to \( \hat{P}_{m_1, m_2, k, k} \) (note, \( n_{m_1 m_2} \) and \( \hat{P}_{m_1, m_2, k, k} \) do not depend on the index \( l \)). In Eq. (34) \( s \) and \( s' \) run over the number of atoms in the cell they belong to \( l \) and \( l' \), respectively, and the sum over \( R_{l'} \) runs over the number of cells (including the original cell, i.e. \( l' = l \)) that are constructed to generate pairs of sites interacting with the inter-site Hubbard \( V_{s's'} \) parameter.

An analogous generalization also has to be applied to the (site-diagonal) perturbing potential, Eq. (25), appearing on the right-hand side of Eq. (29). Its expression now corresponds to the trace of a projector that generalizes Eq. (35) (with \( s' = s \)) to the case with \( q \neq 0 \):

\[
\hat{P}_{m_1, m_2, k+q, k+q} = \hat{S}_{k+q} \left| \bar{\varphi}^{s}_{m_1, k+q} \right> \left< \bar{\varphi}^{s}_{m_1, k+q} \right| \hat{S}_{k+q}.
\]

The functions \( \bar{\varphi}^{s}_{m_1, k} \) are defined in the same way as in the Appendix 1 of Ref. [8].

Finally, the same generalized expression of the lattice-periodic projector on atomic states has to be used in the calculation of monochromatic, \( q \)-dependent components of the linear-response occupation matrices, Eq. (22), that are then employed to calculate the values of the Hubbard \( U \) and \( V \) parameters using Eqs. (15) - (17).

2. PAW

The calculation of the Hubbard parameters with the PAW method is very similar to the one reviewed above
for US PPs. This is so because there are many similarities between US and PAW formalisms, as discussed in detail in Refs. [67, 60]. However, there are a few points that must be clarified. All the equations presented above for US PPs are valid also in the case of PAW, after taking into account the following changes: i) The augmentation functions $Q_{I,J}^{(U)}$ and projector functions $\beta_{\mu}^I$ must be replaced by the ones from the PAW method, ii) in Eq. (29) the terms $\tilde{h}_{k+q,\sigma}^{\nu}$ and $\Delta_{\mu}^{\nu}\tilde{V}_{\text{eff},k+q,k,\sigma}$ have extra contributions (from standard DFPT with PAW) which are defined inside of the augmentation spheres centered about atoms [71].

It is important to remark that our implementation is different from most implementations for DFT+U with PAW (see, e.g., Refs. [72, 74]), because our formalism is based on projecting KS wavefunctions on (orthogonalized) atomic orbitals $\varphi^I$ rather than on projector functions $\beta^I$ (the latter being localized inside the augmentation spheres). One advantage of our formalism is that it allows DFT+U+V to be extended easily to PAW, [Eqs. (7) and (14)].

IV. SELF-CONSISTENT CALCULATION OF HUBBARD PARAMETERS

The increased computational efficiency, the higher level of automation, and user-friendliness promoted by the use of DFPT in the calculation of the Hubbard parameters [15] can also be exploited to make this calculation fully “self-consistent” and to obtain Hubbard parameters that are fully consistent with both the electronic structure of the system and, in addition, with the crystal structure. The idea is to recompute the effective $U$ and $V$ parameters from a DFT+U+V ground state, until the values obtained from the DFPT calculation ($U_{\text{out}}$ and $V_{\text{out}}$) coincide (within a fixed precision $\Delta$) with those used in determining the ground state DFPT is based on ($U_{\text{in}}$ and $V_{\text{in}}$):

$$|U_{\text{out}} - U_{\text{in}}| < \Delta,$$

$$|V_{\text{out}} - V_{\text{in}}| < \Delta.$$  

The convergence (typically in a few cycles) of the iterative procedure in most cases is guaranteed by the observed smooth and monotonic dependence of output interaction parameters ($U_{\text{out}}$, $V_{\text{out}}$) on the input ones ($U_{\text{in}}$ and $V_{\text{in}}$). The iterative procedure is illustrated by the flowchart diagram in Fig. 1 and yields the final “self-consistent” values of the Hubbard interactions, labeled $U_{\text{scf}}$ and $V_{\text{scf}}$.

The idea to compute the Hubbard parameters self-consistently has been explored several times in literature. The first attempt, to the best of our knowledge, was made in Ref. [71] (also involving some of us) where an extrapolation of the linear behavior of $U_{\text{out}}$ (computed from LR-cDFT [42]) as a function of $U_{\text{in}}$ was used to determine the self-consistent value of the Hubbard $U$ through the elimination of the second derivative of the Hubbard correction, consistently with the idea that $U_{\text{scf}}$ should correspond to the curvature of the DFT part only of the total energy. In later works [11, 26, 30, 31, 43, 45, 46, 75] the self-consistent evaluation of the Hubbard parameters was based on an iterative recalculation of their values, each step using the parameters determined at the previous one (or a linear combination of those computed at previous steps). The use of LR-cDFT (or DFPT) to re-calculate iteratively the Hubbard parameters until self-consistency is straightforward. However, in order to avoid that the Hubbard correction responds to the perturbation, thus spuriously contributing to the calculation of the total energy curvature [42], it is important to maintain the Hubbard potential unchanged (and equal to its self-consistent unperturbed value) during the iterative solution of linear-response equations [48], as was discussed above. This is the reason why no Hubbard response potential is included on the right-hand side of Sternheimer equations [18], [24] and [29].

The procedure described to this point obtains the self-consistent values of $U$ and $V$ for a given crystal structure. When structural optimization is necessary it is obviously crucial to obtain full consistency of the final Hubbard parameters with the crystal geometry as well. The importance of the consistency of the Hubbard parameters

![Flowchart](https://via.placeholder.com/150)

FIG. 1: A protocol for the calculation of self-consistent Hubbard parameters $U_{\text{scf}}$ (on-site) and $V_{\text{scf}}$ (inter-site).
with the crystal structure has already been illustrated by some recent works involving the authors [46, 47, 49]. For this reason the flowchart in Fig. 1 also contains a structural relaxation step.

In summary, the procedure to compute $U_{\text{scf}}$ and $V_{\text{scf}}$ is as follows:

- **Step 1.** Set up initial crystal structure for the system of interest and choose initial values for $U$ and $V$ (zero initial values can be used);
- **Step 2.** Perform a structural optimization using DFT+$U$+$V$ with the current values of $U$ and $V$;
- **Step 3.** Perform a self-consistent field (SCF) ground state calculation using DFT+$U$+$V$ with the current values of $U$ and $V$;
- **Step 4.** Perform a DFPT calculation to determine new values of Hubbard parameters $U$ and $V$;
- **Step 5.** Return to step 2 with updated values of $U$ and $V$ and iterate the procedure until the point when the variation of the Hubbard parameters and of the crystal structure are both within fixed thresholds.

The current workflow for the calculation of $U_{\text{scf}}$ and $V_{\text{scf}}$ can be easily implemented and automatized. Since the Hubbard parameters depend on many computational details (chemical composition, choice of localized functions for projectors, xc functional, pseudopotentials, oxidation state, etc.), having a fully automated workflow for calculation of $U_{\text{scf}}$ and $V_{\text{scf}}$ is indispensable for the high-throughput materials’ screening.

V. TECHNICAL DETAILS

In order to exemplify and benchmark the application of the DFPT approach described here we chose MnPO$_4$ and LiMnPO$_4$ as test cases. In this section we review the technical settings of these calculations. The DFPT approach for calculations of Hubbard parameters with US PP and PAW discussed here has been implemented in the QUANTUM ESPRESSO distribution [76, 78] and has been released with version 6.6 [70].

All calculations are performed using the plane-wave (PW) pseudopotential method and the xc functional is constructed using spin-polarized GGA with the PBEsol prescription [80]. Pseudopotentials are chosen based on the SSSP library 1.1 (efficiency) [81, 82]: we have used US PP and PAW [83] from the Pslibrary 0.3.1 and 1.0.0 [84, 85] and the GBRV library 1.2 and 1.5 [86]. The crystal structure is optimized at three levels of theory (DFT, DFT+$U$, and DFT+$U+V$) using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [87], with a convergence threshold for the total energy of $5 \times 10^{-6}$ Ry and for forces of $5 \times 10^{-5}$ Ry/Bohr. We used an antiferromagnetic ordering for both materials (labeled “AF1” in Ref. [46]). To construct the projectors $\varphi^I$ of the Hubbard manifold [see Eq. (14)] we have used atomic orbitals which are orthogonalized using Löwdin’s method [88, 89]; structural optimizations using DFT+$U$ and DFT+$U+V$ are performed using orthogonalized atomic orbitals as described in detail in Ref. [61]. KS pseudo-wavefunctions and potentials are expanded in PWs up to a kinetic-energy cutoff of 90 and 1080 Ry, respectively, for structural optimization, and of 65 and 780 Ry, respectively, for calculation of Hubbard parameters and voltages.

The DFPT calculations of Hubbard parameters (for production purposes) are performed using the uniform Γ-centered k and q point meshes of size $3 \times 4 \times 5$ and $1 \times 2 \times 3$, respectively, which give an accuracy of 0.01 eV for the computed values of $U$ and $V$. Unit cells with four formula units are used, containing 24 atoms in the case of MnPO$_4$ and 28 atoms in the case of LiMnPO$_4$. The linear-response KS equations [20] are solved using the conjugate-gradient algorithm [90] and the mixing scheme of Ref. [91] for the response potential to speed up convergence.

The DFPT calculations of Hubbard parameters (for benchmarking purposes) are performed using uniform Γ-centered k and q point meshes of size $3 \times 4 \times 6$ and $1 \times 2 \times 3$, respectively, and the same unit cells as described above. The equivalent LR-cDFT calculations of $U$ and $V$ were performed using finite differences on $1 \times 2 \times 3$ supercells (resulting in 144 and 168 atoms for MnPO$_4$ and LiMnPO$_4$, respectively) whose Brillouin zone was sampled using a correspondingly coarser Γ-centered $3 \times 2 \times 2$ k point mesh. For LR-cDFT, the strength of the perturbation is chosen to be $\pm 0.05$ eV (see Ref. [42] for more details).

The data used to produce the results of this work are available in the Materials Cloud Archive [92].

VI. RESULTS AND DISCUSSION

A. Benchmark of DFPT versus LR-cDFT

In this section we present a validation of the analytical formulas for DFPT presented in Sec. [11] and their numerical implementation, in the framework of US PP and PAW. For this purpose, we make a comparison with the calculations performed using the well-established LR-cDFT approach of Ref. [42].

As described in Sec. [V] DFPT and LR-cDFT calculations are set up under equivalent conditions so that they ought to give the same values of $U$ and $V$. For more details about the equivalence between these two methods we refer the reader to Ref. [48]. Table 1 shows the comparison of Hubbard parameters computed from these two approaches for MnPO$_4$ and LiMnPO$_4$. The calculations are performed in a “one-shot” fashion, i.e. without performing the self-consistency loop as described in Sec. [V]; our goal here is not to compute $U$ and $V$ self-consistently (this will be discussed in Sec. [VI]) but to validate the
In this section we showcase the self-consistent evaluation of Hubbard parameters $U$ and $V$ for MnPO$_4$ and LiMnPO$_4$ using the workflow described in Sec. IV. The results are shown in Fig. 2.

We can see that after just a few iterations (typically 2 or 3) the Hubbard parameters are already within 0.1 eV from the converged value. We remind here that each iteration requires a structural optimization, a subsequent ground state calculation, and a calculation of Hubbard parameters using DFPT. The first iteration is based on an uncorrected DFT calculation ($U = V = 0$) of the equilibrium structure, while in all subsequent steps the DFPT evaluation of the Hubbard parameters is based on DFT+$U$ or DFT+$U$+$V$ calculations with $U$ and $V$ determined in the previous step.

As can be seen in Fig. 2, the variations of both $U$ and $V$ is in general non-monotonic, and the converged values can be either higher or lower than their values obtained at the first iteration, i.e. obtained from the uncorrected ground state. More specifically, the converged $U$ for LiMnPO$_4$ is about 1 eV smaller than its value at the first iteration, while the variation for MnPO$_4$ is less pronounced (especially with DFT+$U$+$V$). On the other hand, Hubbard $V$ presents much smaller variations – typically within 0.2 eV of their value at the first iteration – and, in addition, $V$ for different pairs of Mn and O atoms typically show a similar convergence trend.

The structural optimization included in the self-consistent procedure (see Fig. 1) is of crucial importance for determining the final values of the Hubbard parameters. This certainly enhances the variation of $U$ and $V$ during the self-consistent cycle due to their sensitivity to the local chemical environment of the Hubbard atoms and to the consequent dependence on the interatomic distances, lattice parameters, cell geometry, and symmetry. We argue that including the structural optimization step is crucial to obtain Hubbard $U$ and $V$ which are fully converged.

### Table I: Comparison of the Hubbard parameters $U$ and $V$ (in eV) computed using LR-cDFT and DFPT, for MnPO$_4$ and LiMnPO$_4$.

| Method        | Hubbard parameters | MnPO$_4$    | LiMnPO$_4$  |
|---------------|---------------------|-------------|-------------|
|               |                     | LR-cDFT     | DFPT        | LR-cDFT     | DFPT        |
| DFT+$U$       | $U$(Mn)             | 6.215       | 6.214       | 5.401       | 5.400       |
|               | $V$(Mn-O$_1$)       | 1.193       | 1.193       | 0.638       | 0.638       |
| DFT+$U$+$V$   | $V$(Mn-O$_2$)       | 1.214       | 1.214       | 0.907       | 0.907       |
|               | $V$(Mn-O$_3$)       | 1.090       | 1.090       | 0.926       | 0.926       |
|               | $V$(Mn-O$_4$)       | 0.666       | 0.666       | 0.539       | 0.539       |

As can be seen from Table I, the agreement between Hubbard parameters $U$ and $V$ computed using DFPT and LR-cDFT is excellent for both cases, and in line with the benchmark for the NC PPs implementation discussed in Ref. [48]. The on-site $U$ for Mn(3d) and the inter-site $V$ between Mn(3d) and O(2p) states agree within $10^{-3}$ eV. The level of agreement could be improved even further by reducing the numerical noise through tighter convergence parameters; however, such accuracy on Hubbard parameters is not needed for any practical application where one wants parameters converged to 0.01–0.1 eV. It is worth noting that in MnPO$_4$ and LiMnPO$_4$ there are four inequivalent types of oxygen atoms (we label them as O$_1$, O$_2$, O$_3$, and O$_4$), and this is the reason why we obtain four values of inter-site Hubbard $V$ parameters between those and the neighbor transition-metal center (Mn atom). For different pairs of atoms, the Hubbard $V$ parameters are different due to variation in inter-atomic distances and local chemical environment (electronic screening), reminding the importance of locally sensitive Hubbard parameters.

Even though the systems used here for benchmark purposes are insulating (even at the DFT level), the extension of DFPT to metals is needed for systems that are metallic (and possibly become insulating after the application of the Hubbard corrections). Such benchmark will not be discussed here, but it has also been investigated in detail, finding excellent agreement between DFPT and LR-cDFT.

All the results discussed above lead us to conclude that the DFPT formalism is correctly extended to US PPs and PAW, and can be reliably used for the calculations of both on-site $U$ and inter-site $V$. Now we can proceed to the self-consistent evaluation of Hubbard parameters using the protocol described in Sec. IV.
FIG. 2: Convergence of the Hubbard parameters $U$ and $V$ during their self-consistent evaluation from DFPT calculations based on DFT+$U$ and DFT+$U+V$. Results are presented for both MnPO$_4$ (left column), and LiMnPO$_4$ (right column). On-site $U$ refers to Mn(3$d$) states while inter-site $V$’s are used between nearest-neighbor pairs of Mn(3$d$) and O(2$p$) states (each Mn being coordinated by four inequivalent O neighbors). All calculations are based on a basis set of orthogonalized atomic orbitals for the Hubbard manifold.

consistent with the crystal structure.

The self-consistent Hubbard parameters $U_{\text{scf}}$ and $V_{\text{scf}}$ are indicated in Figs. 3(a)–(f) [at iteration 4], and these values will be used in the next section for the discussion of structural properties of MnPO$_4$ and LiMnPO$_4$, and for the evaluation of the voltage of a Li$_x$MnPO$_4$-based cathode versus a standard Li/Li$^+$ reference.

C. Structural properties and energetics

The detailed investigation of structural, electronic, and magnetic properties of MnPO$_4$ and LiMnPO$_4$ was already performed in great detail by some of us in a previous study [46]. Here, we will discuss some improvements that we obtained thanks mainly to a more accurate evaluation of the Hubbard parameters achieved with the DFPT implementation, and a more consistent way to perform the structural optimization.

In fact, in Ref. [46] the calculation of Hubbard parameters was performed using LR-cDFT with orthogonalized atomic orbitals, while structural optimizations were performed using non-orthogonalized atomic orbitals, due to the lack of implementation of Hubbard forces and stress with orthogonalized atomic orbitals. Although good agreement with experiments was obtained for various properties using the DFT+$U+V$ functional, the use of different Hubbard manifolds for the calculation of $U$ and $V$ on one hand and for the structural optimization on the other hand is not completely justified. Here, instead, we make use of a recent extension and implementation of Hubbard forces and stresses based on orthogonalized atomic orbitals [61]. Moreover, instead of LR-cDFT as in Ref. [46], we use DFPT for the calculation of the Hubbard $U$ and $V$ parameters using orthogonalized atomic orbitals that, while equivalent to LR-cDFT (see Sec. VII A and Ref. [48]), offers a better control on the numerical accuracy and on the convergence of the Hubbard param-
TABLE II: The equilibrium lattice parameters (LP) $a$, $b$, and $c$ (in Bohr) of LiMnPO$_4$ and MnPO$_4$ computed using DFT, DFT+$U$, and DFT+$U$+$V$ with $U_{\text{scf}}$ and $V_{\text{scf}}$ determined as explained in Sec. VIIB. The experimental data is from Ref. [94] (superscript $a$) and Ref. [95] (superscript $b$).

| Material | $a$ (Bohr) | DFT | DFT+$U$ | DFT+$U$+$V$ | Expt.
|----------|------------|-----|---------|-------------|-------
| LiMnPO$_4$ | 19.61 | 19.80 | 19.79 | 19.76$^a$, 19.71$^b$ |
| b/a | 0.58 | 0.58 | 0.58 | 0.58$^b$ |
| c/a | 0.46 | 0.45 | 0.45 | 0.45$^a$ |
| MnPO$_4$ | 18.40 | 18.52 | 18.46 | 18.31$^b$ |
| b/a | 0.61 | 0.61 | 0.61 | 0.61$^b$ |
| c/a | 0.50 | 0.50 | 0.50 | 0.49$^b$ |

FIG. 3: Voltages (in V) in Li$_x$MnPO$_4$ (vs. Li/Li$^+$) computed using DFT, DFT+$U$, and DFT+$U$+$V$ with $U_{\text{scf}}$ and $V_{\text{scf}}$ determined in Sec. VIIB. The experimental data is from Ref. [96].

VII. CONCLUSIONS

We have presented a generalization of the density-functional perturbation theory approach to the linear-response calculation of both on-site $U$ and inter-site $V$ Hubbard parameters, using ultrasoft pseudopotentials and the projector-augmented wave method. This formalism is applicable to both insulating and metallic ground states, and it does not require the use of computationally expensive supercells with localized perturbations; instead, it is based on calculating the linear response of systems to monochromatic (i.e., wavelength-specific) perturbations inexpensively applied to primitive unit cells [48]. The work also discusses and applies an iterative procedure to compute the Hubbard parameters in full consistency with both the electronic and crystal structures. Moreover, the level of consistency is improved compared to previous works by the application of a recently developed algorithm [61] for the calculation of Hubbard forces and stresses using orthogonalized atomic orbitals as a basis set for the Hubbard manifold.

The new extension of DFPT to US PPs and PAW has been benchmarked against the supercell LR-cDFT approach for LiMnPO$_4$ and MnPO$_4$; the fully lithiated and delithiated members of a cathode material for Li-ion batteries. An excellent agreement is achieved for the Hubbard parameters $U$ and $V$ between the two equivalent techniques, which validates the correctness of the derivation and implementation of the present extension of the DFPT approach to the calculation of Hubbard parameters. The equilibrium lattice parameters and average voltages computed with the DFT+$U$+$V$ approach are in good agreement with experiments, as in Ref. [46], while those obtained with DFT+$U$ are sensibly improved with respect to the previous study. This latter outcome is the result of the consistency achieved between Hubbard parameters and the crystal structure due to the calculation of atomic forces and stresses on a Hubbard manifold of orthogonalized atomic orbitals [61].

What are the reasons for the accuracy of DFT+$U$+$V$
in describing complex materials? This approach does not actually cure correlation shortcomings — strong correlations are really challenging. What it does, very well, is to cure major shortcomings in the energetics that many strongly-correlated systems have, originating in strong self-interaction errors driven by very localized $d$ and $f$ electrons. In this respect, DFT+U and DFT+$U+V$ correct self-interactions in similar ways to hybrid functionals [2], but with a strength that is, thanks to the linear-response approach adopted, sensitive to the electronic-structure environment of the system at hand, and thus ultimately both accurate and efficient. Incidentally, for these reasons these Hubbard functionals can also be applied to molecular systems [7, 44] where there is only a single transition-metal atom, and thus no multi-site correlations.

Finally, it is important to mention that the new framework based on DFPT is implemented in the open-source QUANTUM ESPRESSO distribution [76, 78] and is publicly available to the community at large. This approach, simple and accurate, allows one to perform simulations for complex transition-metal and rare-earth compounds, which are challenging for standard DFT. Notably, it can be easily incorporated in high-throughput workflows for simulations of thousands of materials, which could even be used to machine learn Hubbard parameters, with straightforward applications for data-driven materials modelling. Ultimately, we believe that this approach allows reliable, robust, and computationally affordable simulations to understand, predict, design, and discover novel materials.

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Appendix A: DFT+$U+V$ using the PAW method

In this appendix we discuss in more detail how DFT+$U+V$ is used within the PAW method and its similarities to the case when US PPs are used.

In the PAW method, the KS all-electron wavefunctions $\Psi_{v \kappa \sigma}^\circ$ are reconstructed from the KS pseudo-wavefunctions $\psi_{v \kappa \sigma}^\circ$ as [56]:

$$\Psi_{v \kappa \sigma}^\circ (r) = \psi_{v \kappa \sigma}^\circ (r) + \sum_{J \mu} \left[ \phi_{J \mu}^\circ (r) - \tilde{\phi}_{J \mu}^\circ (r) \right] \langle \beta_{J \mu}^\circ | \psi_{v \kappa \sigma}^\circ \rangle ,$$

(A1)

where $\phi_{J \mu}^\circ$ and $\tilde{\phi}_{J \mu}^\circ$ are the all-electron and pseudo partial waves (coinciding outside augmentation spheres), respectively, obtained from the PAW PPs. A similar expression holds for the all-electron atomic wavefunctions $\Phi_{I}^\circ$ that are obtained from the atomic pseudo-wavefunctions $\varphi_{I \mu}^f$ as:

$$\Phi_{I}^f (r) = \varphi_{I \mu}^f (r) + \sum_{J \mu} \left[ \phi_{J \mu}^\circ (r) - \tilde{\phi}_{J \mu}^\circ (r) \right] \langle \beta_{J \mu}^\circ | \varphi_{I \mu}^f \rangle .$$

(A2)

From these expressions it is easy to compute (keeping in mind that $\langle \beta_{J \mu}^\circ | \tilde{\phi}_{J \mu}^\circ \rangle = \delta_{J \mu}$ within the augmentation spheres [56]) the scalar product between the all-electron KS and atomic wavefunctions:

$$\langle \Psi_{v \kappa \sigma}^\circ | \Phi_{I}^f \rangle = \langle \psi_{v \kappa \sigma}^\circ | \varphi_{I \mu}^f \rangle + \sum_{J \mu} \langle \psi_{v \kappa \sigma}^\circ | \beta_{J \mu}^\circ \rangle \times \left[ \langle \phi_{J \mu}^\circ | \varphi_{I \mu}^f \rangle - \langle \tilde{\phi}_{J \mu}^\circ | \varphi_{I \mu}^f \rangle \right] \langle \beta_{J \mu}^\circ | \varphi_{I \mu}^f \rangle = \langle \psi_{v \kappa \sigma}^\circ | \tilde{S} | \varphi_{I \mu}^f \rangle ,$$

(A3)

where $\tilde{S}$ is the overlap matrix defined in Eq. (10), with the coefficients $q_{I \mu}^{\gamma(I)}$ given by $\langle \phi_{J \mu}^\circ | \varphi_{I \mu}^f \rangle - \langle \tilde{\phi}_{J \mu}^\circ | \varphi_{I \mu}^f \rangle$. The generalized occupation matrices thus result:

$$n_{m_{1}m_{2}}^{J \sigma} = \sum_{J \mu} \sum_{k} \bar{\Theta}_{v \kappa \sigma} \langle \Psi_{v \kappa \sigma}^\circ | \Phi_{I_{m_{2}}^f} \rangle \langle \Phi_{I_{m_{2}}^f} | \Psi_{v \kappa \sigma}^\circ \rangle = \sum_{J \mu} \sum_{k} \bar{\Theta}_{v \kappa \sigma} \langle \psi_{v \kappa \sigma}^\circ | \tilde{P}_{I_{m_{2}}^f} \rangle \langle \tilde{P}_{I_{m_{2}}^f} | \psi_{v \kappa \sigma}^\circ \rangle ,$$

(A4)

where the projector $\tilde{P}_{I_{m_{2}}^f}$ is expressed in exactly the same way as for US PPs:

$$\tilde{P}_{I_{m_{2}}^f} = \tilde{S} | \varphi_{I_{m_{2}}^f} \rangle \langle \varphi_{I_{m_{2}}^f} | \tilde{S} ,$$

(A5)

but with $\tilde{S}$ defined in terms of augmentation and projector functions from the PAW scheme.

Appendix B: Bloch sums

Similarly to the Appendix 1 of Ref. [49], we define here Bloch sums and inverse Bloch sums of projector functions as, respectively,

$$\tilde{\beta}_{\mu_{i} k}^{s} (r) = \frac{1}{\sqrt{N_{k}}} \sum_{R_{i}} e^{i k \cdot R_{i}} \beta_{\mu_{i}} (r - R_{i}) ,$$

(B1)

and

$$\beta_{\mu_{i}}^{s} (r - R_{i}) = \frac{1}{\sqrt{N_{k}}} \sum_{k} e^{-i k \cdot R_{i}} \tilde{\beta}_{\mu_{i} k}^{s} (r) .$$

(B2)
The functions $\tilde{\gamma}^s_{\mu,k}(r)$ are Bloch-like functions and, hence, they can be written as:

$$\tilde{\gamma}^s_{\mu,k}(r) = \frac{1}{\sqrt{N_k}} e^{i k \cdot r} \tilde{\gamma}^s_{\mu,k}(r),$$  \hspace{1cm} (B3)

where

$$\tilde{\gamma}^s_{\mu,k}(r) \equiv e^{-i k \cdot r} \beta^s_{\mu,k}(r - \tau_s).$$  \hspace{1cm} (B4)

The augmentation functions, $Q^s_{\mu\nu}(r) \equiv Q^s_{\mu\nu}(r - \mathbf{R}_i)$, can also be represented using Bloch sums and inverse Bloch sums, respectively, as:

$$Q^s_{\mu\nu,k}(r) = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}_i} e^{i k \cdot \mathbf{R}_i} Q_{\mu\nu}(r - \mathbf{R}_i),$$  \hspace{1cm} (B5)

and

$$Q_{\mu\nu}(r - \mathbf{R}_i) = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} e^{-i k \cdot \mathbf{R}_i} \tilde{Q}^s_{\mu\nu,k}(r).$$  \hspace{1cm} (B6)

Similarly to $\beta^s_{\mu,k}(r)$ [see Eq. (B3)], the functions $\tilde{Q}^s_{\mu\nu,k}(r)$ are Bloch-like functions, and, therefore, they can be written as:

$$\tilde{Q}^s_{\mu\nu,k}(r) = \frac{1}{\sqrt{N_k}} e^{i k \cdot r} \tilde{Q}^s_{\mu\nu,k}(r),$$  \hspace{1cm} (B7)

where

$$\tilde{Q}^s_{\mu\nu,k}(r) \equiv e^{-i k \cdot \tau_s} Q^s_{\mu\nu,k}(r - \tau_s).$$  \hspace{1cm} (B8)

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In order to clarify the meaning of $\hat{P}_{\upsilon k, \upsilon' k}$ and $\hat{\Omega}_{\upsilon k, \upsilon' k}$, it is useful to consider the case of gapped systems, where the smooth step-like functions $\tilde{\theta}$ and $\tilde{\theta}$ are replaced by sharp step functions and the summations in Eqs. (29) and (27) are limited to occupied states: in this case $\hat{P}_{\upsilon k, \upsilon' k}$ and $\hat{\Omega}_{\upsilon k, \upsilon' k}$ become true projectors on empty (conduction) and occupied (valence) states manifolds, respectively.
We used the following pseudopotentials: 0.pbesol-n-rrkjpav.psl.0.1.UPF (PAW), mn.pbesol_v1.5.uspp.F.UPF (US), P.pbesol-n-rrkjpav.psl.1.0.0.UPF (US), and li.pbesol_v1.4.uspp.F.UPF (US).

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