A self-consistent ground-state formulation of the first-principles Hubbard U parameter validated on one-electron self-interaction error

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In electronic structure methods based on the correction of approximate density-functional theory (DFT) for systematic inaccuracies, Hubbard U parameters may be used to quantify and amend the self-interaction errors ascribed to selected subspaces. Here, in order to enable the accurate, computationally convenient calculation of U by means of DFT algorithms that locate the ground-state by direct total-energy minimization, we introduce a reformulation of the successful linear-response method for U in terms of the fully-relaxed constrained ground-state density. Defining U as an implicit functional of the ground-state density implies the comparability of DFT + Hubbard U (DFT+U) total-energies, and related properties, as external parameters such as ionic positions are varied together with their corresponding first-principles U values. Our approach provides a framework in which to address the partially unresolved question of self-consistency over U, for which plausible schemes have been proposed, and to precisely define the energy associated with subspace many-body self-interaction error. We demonstrate that DFT+U precisely corrects the total energy for self-interaction error under ideal conditions, but only if a simple self-consistency condition is applied. Such parameters also promote to first-principles a recently proposed DFT+U based method for enforcing Koopmans' theorem.

I. INTRODUCTION

Approximate density-functional theory (DFT)[1,2] is a central element in the simulation of many-body atomistic systems and an indispensable partner to experiment[3–5]. DFT is prone, however, within its commonplace local-density (LDA)[6], generalized-gradient (GGA)[7], and hybrid[8–10] exchange-correlation (xc) approximations, to significant systematic errors[11,12]. The most widely encountered of these is the many-electron self-interaction error (SIE)[6], or delocalization[12] error, which is manifested as a spurious curvature in the total-energy profile of a system with respect to its total electron number[13]. The SIE contributes to inaccuracies in insulating band gaps[14], charge-transfer energies[15,16], activation barriers[17], binding and formation energies, as well as in spin-densities and their moments. While the nature of SIE is well understood, it remains persistently challenging to reliably avoid its introduction using approximate xc functionals of a computationally tractable, explicit analytical form, even if exact exchange is incorporated (see, e.g., the B3LYP curve in Fig. 2 of Ref. 18).

DFT+U (DFT + Hubbard U)[11,19–23] is a computationally efficient[24] and formally straightforward method that has matured as a corrective approach for SIE in systems where it may be reasonably attributed to particular selected subspaces[25–27]. Originally designed to capture Mott-Hubbard physics in transition-metal oxides[11,20,22,28], it now sees very diverse applications[29–33].

It has gained a transparent interpretation as an efficient corrective method for SIE particularly since the work of Kulik, Cococcioni, and co-workers in Ref. 25. The DFT+U corrective energy term is often invoked in its rotationally-invariant, simplified form[23,25,31,34], given by

$$E_U\left[\hat{n}^{I\sigma}\right] = \sum_{I,\sigma} \frac{U^I}{2} \text{Tr}\left[\hat{n}^{I\sigma} - \hat{n}^{I\sigma}\hat{n}^{I\sigma}\right], \qquad (1)$$

where the density-matrices $\hat{n}^{I\sigma} = \hat{P}^I \hat{\rho}^\sigma \hat{P}^I$ are those for the subspaces I over which the SIE is to be corrected. Here, the Kohn-Sham density-matrix $\hat{\rho}^\sigma$ corresponds to the spin indexed by σ, which we hereafter suppress for simplicity, and the idempotent subspace projection operators $\hat{P}^I = \sum_m |\varphi_m^I\rangle\langle\varphi^{Im}|$ are usually built from fixed, spin-independent, orthonormal, localized orbitals, which may also be nonorthogonal[35] and self-consistent[36].

The quadratic term of Eq. 1 alters the intra-subspace self-interaction, on a one-electron basis in the frame of the individual orthonormal eigenstates of $\hat{n}^I$, which may generally be expected to change as a result. The linear term then imposes the condition that the correction to the total-energy should vanish for each subspace eigenstate as its corresponding eigenvalue n_i^I approaches zero or one, implying that the xc functional is assumed to be correct for such eigenstates. This mirrors the well-known result that the total-energy of open systems at integer filling is reasonably well described by conventional approximate xc functionals[37]. While the linear term does not directly affect the SIE explicitly, it represents an important boundary condition on the SIE correction. Simultaneously , the corresponding correction to the potential $\hat{v}_U^I = U^I(\hat{1} - 2\hat{n}^I)/2$ vanishes at eigenvalues of one-half

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and, when a Kohn-Sham gap is symmetry-allowed, the occupancy-dependence of the potential acts to energetically split states lesser and greater in occupancy than one-half by an energy interval on the order of U[29].

A. A one-electron litmus test: how DFT+U affects H_2^+

As it exhibits no multi-reference or static correlation error effects, by definition, but a straightforwardly variable bonding regime, the dihydrogen cation H_2^+ is perhaps the ideal system for the study of pure SIE, also known as delocalization error[12]. It serves as a convenient test bed for the exploration of system-specific additive corrections, such as DFT+U, and more generally for density-functionals which are, at least in part, implicitly defined via parameters to be calculated, such as the self-consistent Hubbard U. Particularly subject to the ideal population analysis and non-overlapping subspace conditions available in the dissociated limit, H_2^+ will allow us to draw firm conclusions regarding the numerous plausible but different strategies currently in use for defining self-consistency over the Hubbard U.

The action of the DFT+U functional under varying bonding conditions may be observed in the dissociation curves of H_2^+ depicted in Fig. 1a. Here, the total-energy error in approximate DFT, specifically the PBE xc-functional[7], is seen to grow significantly with bond-length as the electron count on each atom approaches one-half. The result of the exact xc-functional, in which the Hartree and xc energies and potentials cancel, is indicated by the solid line, and the results of DFT(PBE)+$U = 0, 4, 8$ eV, are indicated by the dashed lines[38]. The Hubbard U parameter required to correct the PBE total-energy to the exact value varies over approximately 8 eV from the fully bonded to dissociated limits, highlighting the importance of chemical environment dependent, and not just species-dependent, U parameters, as previously shown, e.g., in Refs. 39–41.

A critical and perhaps defining characteristic of an SIE-free system is its compliance with Koopmans' condition[42,43], and in a one-electron system such as H_2^+ this implies that the total-energy and the occupied Kohn-Sham eigenvalue ε should differ only by the ion-ion energy. Thus, the dissociation curve of H_2^+ should be equivalently accessible by calculating the total energies for the dimer and its constituent atoms directly, or by using total energies derived from the occupied eigenvalue and the expression $E = \varepsilon + E_{\text{ion-ion}}$. Fig. 1b illustrates the strikingly poor results of DFT+U when combined with this latter procedure[44]. A $U \gtrsim 4$ eV is required for the eigenvalue-derived dissociation curve to exhibit a local minimum. We observe that the non-compliance with Koopmans' condition (disagreement between Figs. 1a and 1b) broadly decreases both with bond-length and with the Hubbard U, but that the effect of DFT+U on the eigenvalue is lost entirely in the dissociated limit since both factors drive the subspace occupancy to $1/2$. Across
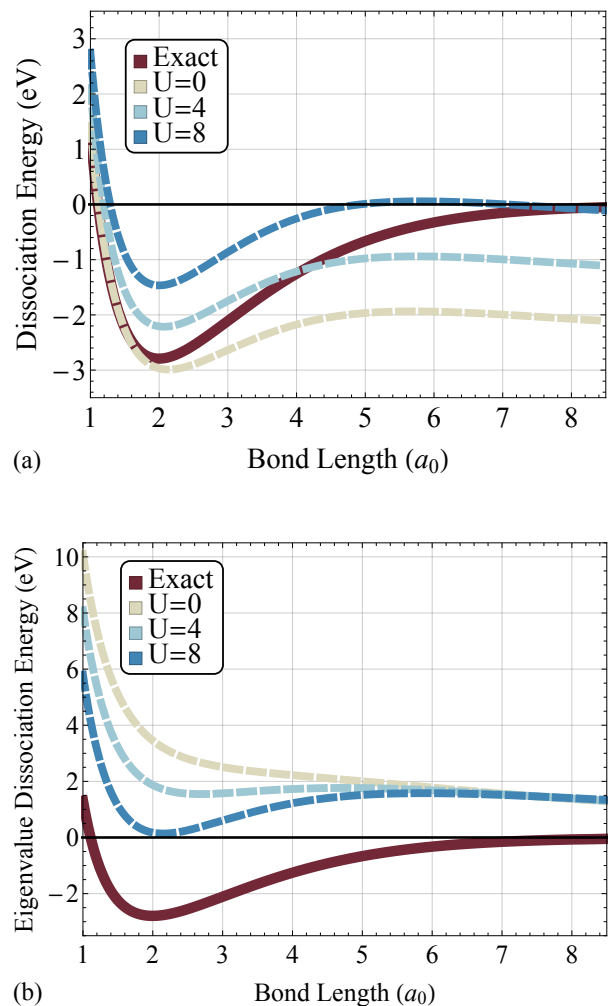

FIG. 1. (Color online) The dissociation energy curve of H_2^+ calculated from (a) the total-energy and (b) the occupied Kohn-Sham eigenvalue using the exact xc-functional (solid), and PBE+U with $U = 0, 4, 8$ eV (dashed). PBE+U successfully resolves the SIE in the total-energy, for a strongly bond-length dependent Hubbard U, but it does not address the inaccuracy in the Kohn-Sham eigenvalue, or non-compliance with Koopmans' condition, which grows with bond-length.

the dissociation curve, the Hubbard U required to enforce compliance with Koopmans' condition, and that needed to attain the exact result typically differ substantially.

The facile correction of the total-energy of this system at each bond length with a varying but reasonable U value sharply contrasts with the inefficacy of DFT+U for fixing the occupied eigenvalue. At dissociation, the latter is not significantly affected by DFT+U, suggesting an intrinsic limitation in the linear term of that correction. We have previously introduced a generalized DFT+U functional in Ref. 45, in which the linear term was amended to enforce Koopmans condition. We will return to put this approach on a first-principles footing using self-consistent variational Hubbard U parameters in Section IV B.

B. The Hubbard U as a first-principles response property: motivations for seeking a variational formalism

The Hubbard U^I are external parameters that define the SIE correction strength applied to each subspace in DFT+U. They may be thought of as subspace-averaged SIEs quantified *in situ*[23,25]. Historically and to this day, the Hubbard U has frequently been determined via the empirical fitting of calculated DFT+U observables to experimental data, typically spectral[46,47]; structural[46,48,49] or energetic[50,51]. This approach is pragmatic and in many cases very successful, but it is clearly inapplicable when the necessary experimental data is unavailable or difficult to measure. If the Hubbard U parameters are instead themselves calculated as properties of the electronic structure, however, becoming no longer free parameters but auxiliary variables, in effect, then DFT+U is restored to a first-principles status. If the Hubbard U are calculated strictly as variational ground-state density-functional properties, even implicitly, i.e., one of the central developments of the present work, then DFT+U as whole becomes a fully self-contained, variational first-principles method. Only under the latter condition would we expect the fully rigorous direct comparability of the total energies, and their derived thermodynamic observables, calculated from different DFT+U calculations with different system-specific U parameters.

In this work, we build upon the very widely-used[4,25,52–63] and successful linear-response method proposed in Ref. 23, in which Cococcioni and de Gironcoli demonstrated that a small number of DFT calculations is sufficient to calculate first-principles Hubbard U parameters by finite-differences, as well as upon the earlier linear-response scheme proposed by Pickett and co-workers[22], and aspects of the modified constrained LDA scheme of Aryasetiawan and co-workers[64]. In this linear-response DFT+U method[23], a small, external uniform perturbation of strength α is applied to the subspace of interest and the interacting response function χ, and its non-interacting Kohn-Sham equivalent χ_0, are computed, respectively, from the first derivatives of the self-consistent and non-self-consistent subspace total occupancies $N^I = \text{Tr}[\hat{n}^I]$ with respect to α. The scalar Dyson equation $U^I = (\chi_0^{-1} - \chi^{-1})^I$ yields U for a single subspace model, which may be further improved under self-consistency[25,65,66]. The Hubbard U parameters appropriate to a generalized model in which inter-subspace parameters V are included[67], as well as the inter-subspace V themselves, may also be calculated[23] by treating the Dyson equation as a site-indexed matrix equation[68].

To date, based on our extensive literature search, the linear-response method has only been used in conjunction with the self-consistent field (SCF) algorithms very typically used to solve the Kohn-Sham equations for smaller isolated and periodic systems. In the SCF case, it is convenient to calculate the non-interacting response function χ_0 following the first iteration of the SCF cycle as prescribed in Ref. 23, i.e., following the initial

charge re-organization induced by the external potential $\hat{v}_{\text{ext}} = \alpha^I \hat{P}^I$, but before any update of the remaining terms in the Kohn-Sham potential is carried out. This technique is impractical to implement, however, in codes that utilize a direct minimization of the total-energy with respect to the density, Kohn-Sham orbitals, or density-matrix to locate the ground-state, since there it is not efficient or customary to nest the density and potential update processes. These codes comprise a growing number of linear-scaling or large-system adapted packages, where explicit Hamiltonian diagonalization is typically avoided altogether where possible, such as ONETEP[69–71], CONQUEST[72,73], SIESTA[74,75], BIGDFT[76], OPENMX[77], and CP2K[78], among others, albeit that the SCF technique may also be available in some of these. We are therefore motivated to seek a linear-response formalism for the Hubbard U that is readily compatible with direct-minimization DFT and large systems, particularly for linear-scaling DFT+U[24].

In this work, we develop and present a minimal revision of the established 'SCF linear-response' approach (terminology specific to this article, introduced for the avoidance of ambiguity) for the Hubbard U parameters, one based on the response of the fully relaxed ground-state density subject to a varying perturbation. We have implemented our 'variational linear-response' method for the U in the linear-scaling direct-minimization DFT package ONETEP[69–71], where the cost of the method itself scales with the number of targeted subspaces to be assessed, multiplied by the total number of atoms present. It is thus readily applicable to systems that are both spatially disordered and electronically challenging. More generally, the variational linear-response method is equally applicable to direct-minimization and SCF DFT codes irrespective of the basis set used, and it may prove helpful in cases where the SCF non-interacting response χ_0 is numerically problematic[29]. We find that it provides a convenient framework in which to analyze a number of different criteria that have been proposed for defining the self-consistent Hubbard U and with it, for the particular case of the variational linear-response Hubbard U at least, we identify a well-defined best choice of self-consistency criterion supported by numerical results.

C. Article outline

In Section II, we investigate the conditions that must hold for a first-principles Hubbard U parameter to correct SIE subspace-locally by means of Eq. 1. Arriving at a simple, variational linear-response formulation in terms of fully-relaxed constrained density and its resulting properties, we make the calculation of Hubbard U parameters accessible to direct-minimization DFT codes. In Section III, we address, for specific case of variational linear-response, the question: which of the previously-proposed and available Hubbard U self-consistency criteria, if any is necessary, is suitable for correcting the

SIE-affected total energy by means of DFT+U? In Section IV, we further analyse our results by means of numerically stringent DFT+U calculations along the dissociation curve of H_2^+, an ideal system for studying one-electron SIE[79,80]. Finally, in our concluding Section VI, we discuss the theoretical relationship between the SCF and variational linear-response formalisms, the relevance to the comparability of total-energies and other thermodynamics quantities from DFT+U calculations with system-specific first-principles Hubbard U parameters, and our outlook on the practicability of such parameters.

II. A VARIATIONAL GROUND-STATE APPROACH TO THE LINEAR-RESPONSE HUBBARD U PARAMETER

In order to calculate the Hubbard U parameter required to subtract the many-electron SIE attributed to a particular subspace, by means of Eq. 1, we may define the parameter for each subspace as the net average electronic interaction acting within it. More specifically, we seek only the interactions at leading order in the subspace density-matrices, that is those coupling to $(n_i^I)^2$, in order to comply with Eq. 1, Thus, for a particular site, we define the U on the basis of the interaction kernel $\hat{f}_{\mathrm{int}} = \delta^2 E_{\mathrm{int}}/\delta\hat{\rho}^2$ only, i.e., not $\hat{g}_{\mathrm{int}} = \delta^3 E_{\mathrm{int}}/\delta\hat{\rho}^3$ etc., where E_{int} is the interacting contribution to the total-energy. Furthermore, we require only the components of the interaction for each subspace that arise due to density variations within it, so that $\hat{f}_{\mathrm{int}}$ must be appropriately projected. In order to illustrate the requirements of such a projection, let us consider some candidate formulae for Hubbard U parameters which do not meet them.

The many-electron SIE of an approximate xc functional, applied to an an open quantum system that does not interact with its bath for particle exchange, is characterized by the spurious non-zero second total-energy derivative with respect to the total occupancy. We may apply this definition to the individual DFT+U subspaces, with occupancies given by $N = \mathrm{Tr}[\hat{n}]$ (suppressing subspace indices), under the reasonable assumption that the subspace-bath interactions are negligible compared to the interactions within the subspace. By defining the Hubbard U for each subspace as the net value of the latter interaction, in a precise sense yet to be determined, the DFT+U functional should act to correct the many-body SIE by subtracting the individual one-electron SIE of each eigenstate of the subspace density-matrix.

Immediately, we may rule out as a Hubbard U parameter the straightforward fully interacting curvature d^2E/dN^2, discussed in Ref. 22, which may be calculated as $-d\alpha/dN$. Here, $\hat{v}_{\mathrm{ext}} = \alpha\hat{P}$ is the external potential inducing the occupancy change. As discussed in Ref. 23, this term comprises a substantial non-interacting contribution, which, in accordance with Dyson equations quite generally, is superfluous to the definition of an interaction and must be subtracted. On the other hand, one may suggest the direct subspace projection

of the interaction kernel (Hartree, xc, any other electronic interaction terms), denoted here for a single site by $\hat{P}(\delta^2 E_{\mathrm{int}}/\delta\hat{n}^2)\hat{P} = \hat{P}\hat{f}_{\mathrm{int}}\hat{P}$. Any bare interaction of this kind neglects the potentially substantial screening effects of density-matrix variations outside the subspace. Thus, it is also an unsuitable starting point for measuring many-body SIE, ruling it out. The U must be bath-screened, yet remain bare of intra-subspace screening.

More interesting is the curvature of the interaction term in the total-energy, $d^2 E_{\mathrm{int}}/dN^2$, and the reasons for its non-suitability are perhaps more subtle. Since the Hellman-Feynman theorem cannot be applied to E_{int} alone, its first total derivative with respect to N, i.e.,

$$\frac{dE_{\mathrm{int}}}{dN} = \frac{\partial E_{\mathrm{int}}}{\partial N} + \mathrm{Tr}\left[\frac{\delta E_{\mathrm{int}}}{\delta\hat{\rho}}\frac{d\hat{\rho}}{dN}\right] \qquad (2)$$

yields not only the partial derivative (vanishing due to no explicit N-dependence in E_{int}, and only an implicit dependence via the changes to the total density-matrix $\hat{\rho}$), but it also comprises a term proportional to the interaction potential $\delta E_{\mathrm{int}}/\delta\hat{\rho}$, bath-screened since $d\hat{\rho}/dN$ couples to the external potential $\hat{v}_{\mathrm{ext}} = \alpha\hat{P}$. The second total derivative $d^2 E_{\mathrm{int}}/dN^2$ incorporates screening again, and the resulting twice-screened objects are unphysical. This problem here is the opposite, in a sense, to that of $\hat{P}\hat{f}_{\mathrm{int}}\hat{P}$, from which one may surmise the correct definition is an intermediate case, where screening effects due to the complement of the subspace at hand should be incorporated, but only once. This motivates us to work not from the energy, but from the potential, i.e., from the unscreened functional derivative of the energy with respect to the density-matrix, and to differentiate by N.

As a functional derivative, i.e., a generalized partial derivative, the interaction term in the Kohn-Sham potential $\hat{v}_{\mathrm{int}} = \delta E_{\mathrm{int}}/\delta\hat{\rho}$ is bare of screening, as is its subspace projection $\hat{P}(\delta E_{\mathrm{int}}/\delta\hat{n})\hat{P} = \hat{P}\hat{v}_{\mathrm{int}}\hat{P}$. The quantity then given by $\mathrm{Tr}[\hat{P}(d\hat{v}_{\mathrm{int}}/d\hat{n})\hat{P}]/\mathrm{Tr}[\hat{P}]^2$ seems to fulfil many of the requirements for a valid Hubbard parameter, namely, that it is a subspace-averaged, once-screened interaction that is non-extensive, i.e. it does not scale extensively with the subspace eigenvalue count $\mathrm{Tr}[\hat{P}]$. In practice, however, the screened kernel $d\hat{v}_{\mathrm{int}}/d\hat{n}$ is cumbersome to calculate, even in orbital-free density-functional theory, and, more importantly, it includes screening effects due to density-matrix rearrangements within the subspace, which make it unsuitable as a quantifier for the subspace-bare interaction to be explicitly corrected by DFT+U. Instead, the object that we required is the average, net, subspace-bare but bath (i.e., environment) screened self-interaction of the subspace. We may meet these specifications by taking the total derivative with respect to the total subspace occupancy N, and, finally, by defining

$$U \equiv \frac{dv_{\mathrm{int}}}{dN}, \quad \text{where} \quad v_{\mathrm{int}} \equiv \frac{\mathrm{Tr}[\hat{v}_{\mathrm{int}}\hat{P}]}{\mathrm{Tr}[\hat{P}]} \qquad (3)$$

is the conveniently calculated, non-extensive, subspace-averaged interaction potential (comprising Hartree, xc,

etc.). Here, since the uniform potential α used in the linear-response method induces to first-order no microscopic density-variations within the subspace except for the uniform shift, the screening processes within the subspaces are effectively suppressed, much as in the constrained random phase approximation[64,81,82].

In practice, as we return to discuss around Eq. 5. the proposed variational linear-response U for a single-site model may still be computed using the Dyson equation, but with the response functions $\chi = dN/d\alpha$ and $\chi_0 = dN/dv_{KS}$, where $v_{KS} \equiv \mathrm{Tr}[\hat{v}_{KS}\hat{P}]/\mathrm{Tr}[\hat{P}]$. Here, both χ and χ_0 are to calculated at the end of the minimization procedure from the same set of constrained ground-state densities defined by α. Thus, while χ is identical to that used in the SCF linear-response introduced in Ref. 23, our χ_0 formula is somewhat different (at least formally, the numerical differences remain unclear). The SCF and variational linear-response formalisms are equally compatible with SCF and direct-minimization DFT, as well as with the matrix Dyson equation required, e.g., for calculating longer-ranged inter-subspace parameters V[67] and their corresponding Hubbard U values.

A. The subspace contribution to total-energy curvature

The subspace contribution to the interacting part of the total-energy SIE, specifically that corresponding to the variational linear-response Hubbard U, is the integral of the the interacting part of the Kohn-Sham potential over the subspace occupancy up to its ground-state value. To the same effect, we may use the negative of the integral over the external potential α needed to fully deplete that occupancy back to zero, as in

$$E_{int}^{SIE}(N) = \int_0^N v_{int}(N')\ dN' \qquad (4)$$
$$= -\int_0^\infty v_{int}(N'(\alpha))\frac{dN'}{d\alpha}\ d\alpha$$
$$= \int_0^\infty v_{int}(N'(\alpha))\left(\left.\frac{d^2 E_{total}}{dN''^2}\right|_{N''(\alpha)}\right)^{-1} d\alpha$$

In the final line, we make the connection to the occupancy curvature of the total-energy E_{total} using the result for the constrained DFT system, $dE_{total}/dN = -\alpha$. Although E_{int}^{SIE} does not appear anywhere in our DFT+U implementation in practice, we emphasise that for a single-site model, in the variational linear-response formalism at least, it is $d^2 E_{SIE}/dN^2 = U$, and not the total-energy curvature $d^2 E_{total}/dN^2 = -\chi^{-1}$, which yields the parameter required for DFT+U. Considering the difference of the energy curvatures ascribed to the bath-screened subspace and the overall global system, both as a function of subspace occupancy, we find that $d^2(E_{total} - E_{SIE})/dN^2 = -\chi^{-1} - U = -\chi_0^{-1} \geq 0$, where the latter inequality was proven in Ref. 83. This result is reminiscent of the findings of Kulik *et al.* in

Ref 27, to wit, that while the application of DFT+U can only be expected to mitigate subspace SIE, and at the very least it cannot disimprove the global SIE, albeit for a different sense of global pertaining to total occupancy.

The quantity E_{int}^{SIE} differs from the full subspace contribution to the total-energy SIE by a non-interacting contribution required to restore Koopmans' condition. It is interesting to assume, for a moment, that the SIE kernel $U = dv_{int}/dN$ is Hartree-dominated and hence approximately constant, so that $v_{int}(N) \approx UN$ and $E_{int}^{SIE} \approx UN^2/2$. If we further assume that the subspace is SIE-free at the nearest integer occupancy, N_0, as well as at $N_0 \pm 1$, with a linear (i.e., non-interacting) interpolation term being required between these points, then we may make the curvature-preserving modification $E^{SIE} \approx (U/2)[(N-N_0)^2 - |N-N_0|]$. Taking the negative of this energy to estimate a total-energy correction, and considering single-orbital, single-spin sites, we effectively re-derive the E_U of Eq. 1. Even non-self-consistently, this turns out to be an acceptable energy correction for H_2^+ in the dissociated limit, with two subspaces of $U \approx 8$ eV and $N \approx 1/2$, yielding $-E_{SIE} \approx 2$ eV $\approx E_{exact} - E_{PBE}$.

III. SELF-CONSISTENCY OVER THE HUBBARD U

Beginning with the work of Kulik and co-workers in Ref 25, and in later works[65–67], it has been demonstrated that a self-consistently calculated U can be required for certain systems where the nature of the electronic states (and corresponding response properties) in the DFT+U ground-state differ qualitatively from those of the DFT ground-state[11,34,84]. In self-consistency schemes generally, incremental values of U_{in} are applied to the subspace at hand, with varying ground-state orbitals and densities as a result, and a new first-principles U_{out} is computed for each U_{in}. The numerical relationship $U_{out}(U_{in})$ is then used to select the self-consistent U, using a predefined criterion. Its clear conceptual elegance aside, a self-consistent U has been shown to provide improvements in transition-metal chemistry[26,34,85–91], biological systems[61], photovoltaics[92–94], and high-density energy storage[31]. While many researchers have used an original, linear-extrapolation type U_{scf} in their studies[26,61,85,88–95], others have used the equality between U_{in} and U_{out} as an alternative self-consistency condition[31,34,61,67,87,96]. The majority of published first-principles U calculations involve no self-consistency over the parameter at all, and there may even be a case to be made that none is ordinarily warranted. The resolution of this ambiguity is, in itself, an intriguing open challenge in abstract DFT, but it particularly demands investigation in the present context of the variational linear-response U since, ideally, the optimal scheme to match that method should be established from the outset. On the basis of this study, however, we emphasise that we cannot draw conclusions concerning the self-consistency schemes for U parameters calculated by means of any other methods.

In order to compute variational linear-response U_{out} for a single subspace already subject to a DFT+U term of strength U_{in}, the subspace-averaged interaction v_{int} must incorporate the DFT+U potential $\hat{v}_U$, as well as the usual Hartree + xc term $\hat{v}_{\text{Hxc}}$. Each component in the subspace-averaged interaction potential $v_{\text{KS}} - v_{\text{ext}} \equiv v_{\text{int}} = v_{\text{Hxc}} + v_{U_{\text{in}}}$ must be defined in such a manner that does not scale extensively with the orbital count of the subspace, $\text{Tr}[\hat{P}]$. For Hartree + xc, the appropriate average is $v_{\text{Hxc}} = \text{Tr}[\hat{v}_{\text{Hxc}}\hat{P}]/\text{Tr}[\hat{P}]$ (the operator $\hat{v}_{\text{Hxc}}$ may approximately scale with N but the averaging scheme does not), while the average differential to the external potential is, similarly, $dv_{\text{ext}} = \text{Tr}[d\hat{v}_{\text{ext}}\hat{P}]/\text{Tr}[\hat{P}] = \text{Tr}[d\alpha\hat{P}\hat{P}]/\text{Tr}[\hat{P}] = d\alpha$ by the idempotency of $\hat{P}$. Unlike $\hat{v}_{\text{Hxc}}$, which acts on one state but is generated by all occupied states, the DFT+U potential $\hat{v}_{U_{\text{in}}} = U_{\text{in}}(\hat{P} - 2\hat{P}\hat{\rho}\hat{P})/2$ is intrinsically both specific to and due to each subspace occupancy matrix eigenvector individually. Thus, we find that the simple trace $v_{U_{\text{in}}} = \text{Tr}[\hat{v}_{U_{\text{in}}}] = U_{\text{in}}(\text{Tr}[\hat{P}] - 2N)/2$ is that which scales appropriately with N or, put another way, $v_{U_{\text{in}}}$ would be the average DFT+U potential acting on a subspace eigenvector were there $\text{Tr}[\hat{P}]$ copies of that eigenvector, and thus is comparable with v_{Hxc}. The factor $\text{Tr}[\hat{P}]$ separating the definitions of v_{Hxc} and $\hat{v}_{U_{\text{in}}}$ is consistent with DFT+U correcting the Hartree + xc generated many-body subspace SIE, which is assumed to be proportional to $N^2 \approx (\text{Tr}[\hat{P}]\langle n_i\rangle)^2$, by only $\text{Tr}[\hat{P}]$ one-electron SIE corrector terms on the order of $\langle n_i\rangle^2$. Finally we may write, for the single-site variational linear-response Hubbard U_{out} in the presence of a non-zero U_{in}, that

$$U_{\text{out}} = \chi_0^{-1} - \chi^{-1} = \frac{dv_{\text{KS}} - dv_{\text{ext}}}{dN} = \frac{dv_{\text{int}}}{dN}$$
$$= \frac{dv_{\text{Hxc}}}{dN} - U_{\text{in}} = f_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}) - U_{\text{in}}, \qquad (5)$$

where $f_{\text{Hxc}}^{\hat{P}}(U_{\text{in}}) \equiv dv_{\text{Hxc}}/dN$ is the subspace-averaged, subspace-bare but bath-screened Hxc interaction calculated at the fully-relaxed DFT+U_{in} ground-state.

From Eq. 5 we may readily identify three unique self-consistency criteria. The first is a very plausible self-consistency criterion, first proposed in Ref. 67 and later utilized in Refs. 31 and 34, which requires that $U_{\text{out}} = U_{\text{in}}$ and thus gives $U_{\text{in}} = f_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})/2$. This U_{in}, denoted here as $U^{(1)}$, appears to account for, i.e., cancel away one-half of the subspace SIE that remains at that DFT+U_{in}. The second criterion is given by $U_{\text{out}} = 0$, denoted here by $U^{(2)}$, which dictates that $U_{\text{in}} = f_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})$, implying that U_{in} fully cancels the subspace-related SIE computed at the same DFT+$_{\text{in}}$ ground-state. The third condition, denoted by $U^{(3)}$, matches (albeit with a different underling linear-response procedure) the original self-consistency scheme[25] where it is denoted U_{scf}. Here, the $U_{\text{out}}(0)$ of the DFT+U electronic structure is calculated by a linear-extrapolation of $U_{\text{out}}(U_{\text{in}})$ for sufficiently large U_{in} to obtain a good fit, back to $U_{\text{in}} = 0$ eV.

For our present purposes, it is reasonable to assume that a DFT+U corrected electronic structure has been well-obtained at $U^{(2)}$, and thus performing the linear extrapolation for $U^{(3)}$ around $U^{(2)}$, we find that

$$U^{(3)} = U^{(2)} \left(1 - \frac{df_{\text{Hxc}}^{\hat{P}}}{dU_{\text{in}}}\bigg|_{U^{(2)}} \right). \qquad (6)$$

From this, a clear interpretation of $U^{(3)}$ as screened version of $U^{(2)}$ emerges, in a generalized sense of screening in which, instead of an externally applied potential being attenuated by relaxation of the electronic structure, it is instead the externally applied *interaction correction* which is attenuated. A normal dielectric screening operator measures the rate of change of the potential with respect to an external perturbation, taking the form $\hat{\epsilon}^{-1} = d\hat{v}_{\text{KS}}/d\hat{v}_{\text{ext}} = \hat{1} + \hat{f}_{\text{Hxc}}\hat{\chi}$. A generalized screening function here instead measures the rate of reduction in subspace-averaged SIE with respect to U_{in}, and is given by $\epsilon_U^{-1} = -dU_{\text{out}}/dU_{\text{in}} = 1 - df_{\text{Hxc}}^{\hat{P}}/dU_{\text{in}}$. Therefore, while we require a DFT+U correction with parameter $U^{(2)}$ to cancel the subspace-averaged SIE including all self-consistent response effects in the electronic structure, when we have done so we have in fact removed an SIE (with respect to DFT) of magnitude $U^{(3)} = \epsilon_U^{-1}U^{(2)}$, which is typically smaller in magnitude than $U^{(2)}$. There is a numerically relevant distinction between the external 'bare' U_{in} that we apply using DFT+U, and the 'screened' SIE quantifier U_{out} that we then measure.

The SIE measure $U^{(3)}$, calculated around the $U^{(2)}$ ground-state, is of particular interest, e.g., for quantifying the change in SIE in a subspace in response to an external parameter such as atomic position, or if comparing the SIE of an atom in two different charge states. We also expect $U^{(3)}$ to be suitable as an input Hubbard U parameter for non-self-consistent protocols such as a post-processing DFT+U band-structure correction based on the DFT density, or a DFT + dynamical mean-field theory (DMFT) calculation with no density self-consistency. $U^{(3)}$ linearly accounts for the resistance to SIE reduction that *would* be met were density self-consistency in response to U allowed. On the basis of the above analysis, however, we conclude that the criterion $U^{(2)}$ represents the appropriate self-consistency scheme for the variational linear-response method, wherever the standard self-consistent response of the density occurs upon application of DFT+U. The value of $U^{(2)}$ may be efficiently obtained, e.g., by the bisection method. The three self-consistency conditions are summarized in Table I.

Notation	Criterion	Formula derived from Eq. 5
$U^{(1)}$	$U_{\text{out}} = U_{\text{in}}$	$U_{\text{in}} = f_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})/2$
$U^{(2)}$	$U_{\text{out}} = 0$	$U_{\text{in}} = f_{\text{Hxc}}^{\hat{P}}(U_{\text{in}})$
$U^{(3)}$	$U_{\text{out}}(0)$	$U_{\text{out}}(0) = U^{(2)}(1 - df_{\text{Hxc}}^{\hat{P}}/dU_{\text{in}}|_{U^{(2)}})$

TABLE I. Summary of three first-principles Hubbard U self-consistency criteria derived from Eq. 5.

IV. NUMERICAL RESULTS

A. Self-consistent U schemes applied to dissociating H_2^+

In order to assess the potency of DFT+U for correcting SIE under varying bonding conditions without the complicating effects of static correlation error, we calculated self-consistent Hubbard U values and the resulting DFT+U electronic structure along the binding curve of the dissociating one-electron dimer H_2^+. A further advantage of the one-electron system is that the PBE and exact (i.e., for one electron, simply no Hartree or xc) functionals are available using the same first-principles code and pseudopotential, which ensures the accurate comparability of energies across the parameter space. Stringent numerical conditions were applied, with an extremely accurate small-core norm-conserving PBE pseudopotential and a plane-wave equivalent kinetic energy cutoff of approximately 2650 eV, yielding deviations from 0.5 Ha within w (x) and y (z) on the isolated-atom total-energy and occupied Kohn-Sham eigenvalue, respectively, for the exact (PBE in parentheses) functional. The dissociated limit is of particular interest for confirming the relative appositeness of Hubbard U self-consistency schemes that may yield numerically similar results since, in that limit, the neutral-atom PBE 1s orbitals used to define each of the two DFT+U subspaces spatially overlap (i.e., double-count) and spill the total charge minimally, and the DFT+U population analysis for the PBE dimer becomes ideal. Furthermore, as we approach the dissociated limit, the assumption that each of the two DFT+U subspaces interacts relatively weakly with its bath (in each case, the other atom) becomes increasingly realistic, representing the best available performance of DFT+U using an fixed atomic population analysis (i.e., one that is not dependent on the charge, applied U, or other details of the electronic structure, as Wannier functions are[36,97]).

While conserving the overall charge, the external potential α was varied within the range ±0.05 eV and applied to one atom. DFT+U was applied to both atoms equally, with U_{in} sampled from 0 eV up to the value that yielded $U_{out} = 0$ eV. A typical calculation of U_{out} is shown in the left inset of Fig. 2. For each bond-length, a U_{in} versus U_{out} profile was calculated according to Eq. 5, as illustrated in the right inset of Fig 2 with due care to error accumulation. These profiles were found to remain highly linear across all bond-lengths for this particular system and linear-response methodology, and we note that the slope remained greater than −1, signifying $df_{Hxc}^{\hat{P}}/dU_{in} > 0$ and a 'resistance' to SIE reduction, for all but the small bond-lengths $\lesssim 1.3$ a$_0$ strongly affected by subspace double-counting. The linear fit to $U_{out}(U_{in})$ was then used to evaluate $U^{(1)}$, $U^{(2)}$, $U^{(3)}$, according to Table I, and their values are depicted by dashed, dotted and dot-dashed lines, respectively, in Fig. 2. For each bond-length, we also estimated, by interpolation, the U_{int} (solid line) required to recover the exact total-energy.

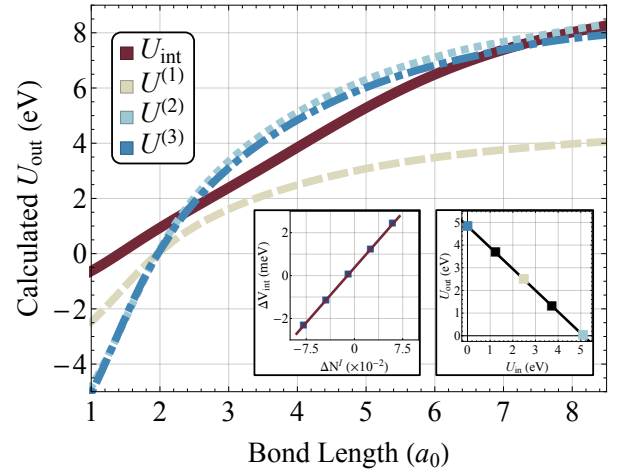The $U^{(2)}$ and $U^{(3)}$ schemes, and particularly the for-

FIG. 2. (Color online) The estimated best U value, U_{int} (solid), for correcting the total-energy SIE in H_2^+, shown with the $U^{(1)}$ (dashed), $U^{(2)}$ (dotted), and $U^{(3)}$ (dot-dashed) values. (Inset left) A sample U_{out} calculation at 4 a$_0$ and $U_{in} = 1.5$ eV. (Inset right) A sample U_{in} vs U_{out} profile used to evaluate $U^{(1)}$, $U^{(2)}$, $U^{(3)}$ (highlighted points), via Table I. $U^{(2)}$ and $U^{(3)}$ approximately equal U_{int} in the dissociation limit, while $U^{(1)}$ is serendipitously more successful at equilibrium and below due to subspace overlap and double-counting.

mer, closely approximate the U_{int} required to correct the SIE in the total-energy in the dissociated limit, whereas $U^{(1)}$ clearly represents an underestimation by a factor of 2, as indicated by Table I. The numerical situation is reversed within the equilibrium bond-length of approximately 2 a$_0$, where $U^{(1)}$ appears to perform better than the alternatives. We emphasise that the latter result is misleading, however, since $U^{(1)}$ performs better at short bond lengths only due to the cancellation of its factor-of-two magnitude reduction with the double-counting effects of spatially overlapping DFT+U subspaces, as well as the breakdown, in the strong-bonding regime, of the subspace-bath separation underpinning DFT+U. This highlights a risk when assessing the relative merits of correction formulae of this kind solely on the basis of numerical results gathered under equilibrium conditions, where bonding or overlap effects complicate the analysis.

The total-energy based dissociation curves of H_2^+ were recalculated using the bond-length dependent $U^{(1)}$ (dashed), $U^{(2)}$ (dotted), and $U^{(3)}$ (dot-dashed), for comparison with the exact total-energy (solid) in Fig. 3. We note that any attempt to extend our bond length interval beyond 8.5 a$_0$ resulted in numerical instabilities due to the near-degeneracy of the Kohn-Sham σ and σ^* eigenstates, and present here are the results only of well-converging calculations. As already suggested by Fig. 2, $U^{(1)}$ fails to correct the SIE in the total-energy at bond-lengths further from equilibrium, whereas $U^{(2)}$ and $U^{(3)}$ provide a more universal correction of the total-energy, becoming acceptable in the dissociation limit. The inset

of Fig. 3 illustrates, however, that the PBE+$U^{(3)}$ scheme, which is numerically equivalent to no Hubbard U self-consistency in this particular system, begins to under-perform with respect to PBE+$U^{(2)}$ in the dissociated limit. The PBE+$U^{(2)}$ total-energy, meanwhile, seems to converge upon the exact total-energy asymptotically. Our results confirm that DFT+U is capable of precisely correcting the total-energy SIE of a one-electron system under ideal population-analysis conditions but only, it seems, when using the simplest self-consistency scheme, $U^{(2)}$. It is clear, notwithstanding, that DFT+U is an efficient and effective corrector for the SIE manifested in the total-energy, as discussed in detail in Refs. [25–27].
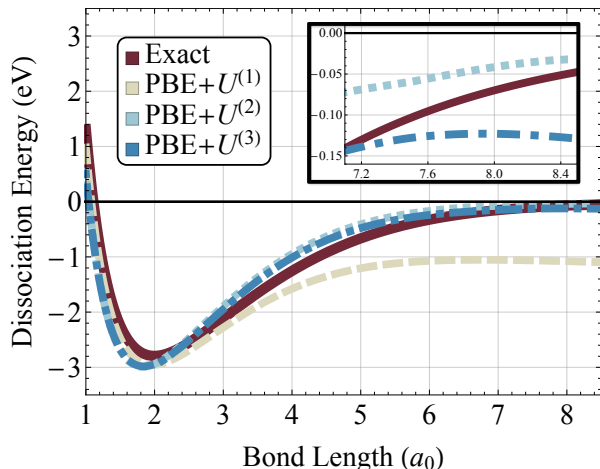

FIG. 3. (Color online) The H_2^+ dissociation curves of the exact functional (solid), PBE+$U^{(1)}$ (dashed), PBE+$U^{(2)}$ (dotted), and PBE+$U^{(3)}$ (dot-dashed). In the dissociated limit (inset), the $U^{(2)}$ result tends asymptotically to the exact one, and the $U^{(3)}$ scheme begins to deviate from it non-negligibly.

B. Restoration of Koopmans' condition: DFT+U_1+U_2

Despite the success of DFT+U in SIE-correcting the total-energy using a suitably calculated U value, the fact remains that it is incapable of simultaneously correcting the highest occupied Kohn-Sham eigenvalue to minus the ionization potential in compliance with Koopmans' condition, as indicated in Fig. 1b. This issue has previously been explored in Ref. [27], and by us in Ref. [45] where we constructed a generalized, two-parameter DFT+U functional, comprising separate parameters for the linear (U_1) and quadratic (U_2) terms. In fact, Eq. 9 of Ref. [45] indicates that if a symmetric system of two one-orbital subspaces (a very good approximation for H_2^+, with approximately constant subspace occupancies N) is Koopmans' compliant (so that the Koopmans' $U_K = 0$), and it is then corrected using DFT+U for the SIE in the total-energy (it is possible for the interaction strength to be inaccurate, but for the system still to comply with Koopmans' condition), then DFT+U will act to spoil

that condition unless $U_1 = 2U_2(N - N^2)/(1 - 2N)$. More pragmatically, we expect the extra degree of freedom furnished by U_1 to be beneficial in cases where the quadratic approximation to the subspace-averaged self-interaction does not remain valid all the way down to the ionized state, which is particularly relevant for H_2^+ since there that state corresponds to the low-density limit. For compliance with Koopmans' condition, it seems unavoidable that data must be collected from both the approximate neutral and ionized (the total energy of which may be sufficient) systems, in order to calculate U_1 and U_2.

We carried out density non-self-consistent DFT+U_1+U_2 calculations on the basis of the PBE total energy and occupied Kohn-Sham eigenvalue, following the formulae given in Ref. [45]. To put the method on a first-principles footing, we used the self-consistent value $U^{(2)}$ to calculate U_1 and U_2, resulting in a density correction to the total-energy summing to $\Delta E = U^{(2)}(N - N^2)$. The corresponding modification to the subspace potentials is given by $\Delta v_U = U^{(2)}(N - N^2) - U_K/2$ where, for this system, $U_K/2 = E_{\text{ion-ion}} - E_{\text{PBE}} + \varepsilon_{\text{PBE}}$. Noting that the correction to the Kohn-Sham eigenvalue ε_{PBE} tends to Δv_U in the dissociated limit where changes to the occupied Kohn-Sham orbital are negligible, there we find that $\varepsilon_{\text{PBE}+U_1+U_2} \equiv \varepsilon_{\text{PBE}} + \Delta v_U = \varepsilon_{\text{PBE}} + \Delta E - (E_{\text{ion-ion}} - E_{\text{PBE}} + \varepsilon_{\text{PBE}}) = -(E_{\text{ion-ion}} - E_{\text{PBE}+U_1+U_2}) \equiv -\text{IP}$, if IP is the ionization potential, i.e., that Koopmans' compliance is restored for a SIE correction strength of $U^{(2)}$. Fig. 4 illustrates the result of this simple technique, which simultaneously reconciles the total energy E and eigenvalue ε derived dissociation curves with the PBE+$U^{(2)}$ dissociation curve of Fig. 3, albeit imprecisely as this is a non-self-consistent post-processing step.

Our results highlights the potential of the DFT+U_1 + U_2 approach and its immediate compatibility with self-consistently calculated Hubbard U parameters. To our knowledge, the SIE of approximate DFT has not previously been simultaneously addressed for the total-energy and the occupied Kohn-Sham eigenvalue using a first-principles correction method of DFT+U type, even for a one-electron system such as this. In the manner in which we have performed it here, non-self-consistent DFT+U_1 + U_2 requires only one total-energy calculation, at the ionized state, on top of the usual apparatus of a linear-response DFT+U calculation, in order to simultaneously, albeit approximately, correct the total energy and the highest occupied Kohn-Sham eigenvalue for SIE. Interesting avenues for the development of this method include its extension to multi-electron, heterogeneous, and non-trivially spin-polarized systems, as well as to perform self-consistency over the density and to lift the fixed-occupancy approximation, as outlined in Ref. [45]. In principle, a further refinement of the method might entail the self-consistent linear-response calculation of U_1 and U_2 separately for the neutral and ionized states.
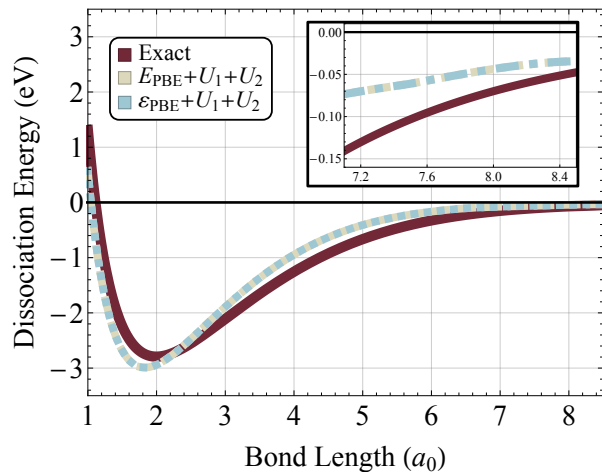
FIG. 4. (Color online) Exact (solid), total-energy based $E_{\mathrm{PBE}+U_1+U_2}$ (dashed), and eigenvalue based $\varepsilon_{\mathrm{PBE}+U_1+U_2}$ (dotted) dissociation energy curves for H_2^+, calculated using DFT+U_1+U_2 as defined in the main text. This method, combined with self-consistently calculated Hubbard U parameters, here of $U^{(2)}$ type, enables the simultaneous SIE correction of the total-energy and Kohn-Sham eigenvalue (to precisely the same accuracy for a one-electron system, as shown).

C. Binding Curve Parameters

In order to further quantify the results of the various Hubbard U self-consistency schemes tested, we determined the equilibrium bond-length R_e, dissociation energy E_D, harmonic frequency ω_e and anharmonicity $\omega_e\chi_e$, corresponding to each, as shown in Table II, by fitting a polynomial about the energy minima. As compared with the experimental data of Ref. 98, the exact calculations perform well in determining the bond-length and harmonicity in particular, with errors that reflect the inaccuracies due to our fitting scheme, finite computational basis set size, core pseudization, and absent physical effects, as well as experimental factors.

The PBE functional overestimates the equilibrium bond-length and dissociation energy, while underestimat-

	R_e	E_D	ω_e	$\omega_e\chi_e$
Experiment[98]	1.988	2.6508	2321.7	66.2
Exact	1.997	2.7922	2323.6	59.9
PBE	2.138	2.9893	1912.0	37.9
PBE+$U^{(1)}$	1.963	2.957(3)	2346(6)	57.7(3)
PBE+$U^{(2)}$	1.827	2.990(3)	2799(5)	81.2(4)
PBE+$U^{(3)}$	1.845	2.985(9)	2721(9)	76.9(7)
PBE+U_1+U_2	1.829	2.990(2)	2810(3)	81.8(6)

TABLE II. Equilibrium bond-lengths R_e (bohr), dissociation energy E_D (eV), harmonic frequencies ω_e (cm^{-1}), and anharmonicities $\omega_e\chi_e$ (cm^{-1}) for each calculation scheme tested, for comparison with experimental values[98].

ing the harmonic frequency and anharmonicity. The various DFT+U schemes tested generally preserve the PBE dissociation energy (N.B., calculated with respect to the exact-functional one-atom total-energy, rather than to the PBE local maximum at 6-7 a_0) but they reduce the bond-length and increase the frequency and anharmonictiy. The $U^{(2)}$, $U^{(3)}$ and U_1+U_2 schemes over-correct the latter three and remain as poorly predictive of the experimental data as the uncorrected PBE is. We attribute this to imperfect DFT+U population analysis at shorter bond-lengths, featuring both double-counting across the two subspaces and spillage, as well as the breakdown of the subspace-bath separation. The double-counting, in particular, is not properly compensated for by self-consistently calculated U parameters, since the formula for U_{out} features no quantification of this effect. The $U^{(1)}$ scheme performs well here, as reflected also in Fig. 2, approximately recovering the exact bond-length, harmonic frequency and anharmonicity. We emphasise that this is due entirely to the $U^{(1)}$ parameter simply being smaller be definition, so that the over-correction due to double-counting is less extreme. It therefore coincides with the exact regime serendipitously, and not by design.

V. THE COMPARABILITY OF DFT+U TOTAL ENERGIES AND THE CONNECTIONS BETWEEN THE SCF AND VARIATIONAL LINEAR-RESPONSE

In this section, we explore the relevance of first-principles calculated Hubbard U values, particularly at self-consistency, to the comparability of the DFT+U total energies across different calculations in which the Hubbard U is separately calculated due to the variation of external parameters such as stoichiometry and crystallographic geometry. We also clarify the technical similarities and differences between SCF linear-response[23] and its derived variational linear-response method.

The open question of the rigorous comparability of DFT+U total-energies that are generated by calculations with different U values, which ordinarily represent external parameters with the same status as ionic positions, is of considerable contemporary relevance. This is demonstrated by recent progress in calculating thermodynamic quantities[41,99–103], in high-throughput materials informatics[104–106], catalysis[62,107–109], and in the study of ion-migration in battery materials[31,47,51,52,54,84,110–112] by means of DFT+U and its related methods.

The variational linear-response definition $U = dv_{\mathrm{int}}/dN$, so-called as it is based on the variational response of the ground-state density, demands that the subspace-averaged non-interacting response $\chi_0 = dN/dv_{\mathrm{KS}}$ is calculated using the same set of ground-state densities, parameterized by the external perturbation strength α, as that used for calculating the interacting response $\chi = dN/d\alpha$. We may therefore write, taking

the limit of small perturbations, that

$$U_{\text{out}} = \chi_0^{-1} - \chi^{-1} = \left.\frac{dv_{\text{KS}}\left[\hat{\rho}\right]}{dN\left[\hat{\rho}\right]}\right|_{\hat{\rho}_0} - \left.\frac{dv_{\text{ext}}\left[\hat{\rho}\right]}{dN\left[\hat{\rho}\right]}\right|_{\hat{\rho}_0}, \quad (7)$$

where $\hat{\rho}_0$ is the unperturbed Kohn-Sham density-matrix. From this, it is clear that $U_{\text{out}}\left[\hat{\rho}_0\right]$ is a ground-state density-functional, albeit not one of an explicit algebraic form. This definition is readily adaptable to orbital-free DFT, in which there is no Kohn-Sham Hamiltonian to diagonalize but only a density (rather than a Kohn-Sham density-matrix) to optimize, and where $\hat{v}_{\text{KS}}$ is replaced by the total potential. If we perform a variational linear-response calculation for a given U_{in}, notwithstanding, then the resulting U_{out} may thought of as a ground-state density functional parameterised by U_{in}. If we can then uniquely determine U_{in} by applying a self-consistency criterion such as $U_{\text{out}} = 0$ eV, we will thereby uniquely determine the self-consistent ground-state DFT+U density-matrix (up to unitary transformations) $\hat{\rho}_0(U_{\text{in}})$, as well as its derived properties such as the total-energy, in terms of the remaining parameters, e.g., ionic positions.

The comparability of total-energies between various crystallographic or molecular structures with differing self-consistent Hubbard U values, and the validity of thermodynamic calculations based on DFT+U, directly follows. In this way, given the underlying explicit algebraic xc functional such as PBE, together with the choice of a set of subspaces to target for SIE correction, DFT+U is elevated to the status of a self-contained orbital-dependent density-functional in its own right, incorporating the Hubbard U as a non-algebraic but readily computable auxiliary ground-state variable.

The SCF[23] and variational linear-response methods are identical in terms of their applied external perturbation, the use of the Dyson equation for multi-site models, and issues of DFT+U population analysis choice and convergence. While they are equally convenient for use with SCF-type DFT solvers, the variational approach is likely to be more convenient for use with direct-minimization solvers. They are also perfectly identical insofar as the calculation of χ is concerned. They differ only in the definition and set of densities used to calculate the subspace-averaged non-interacting response χ_0.

A calculation of the non-interacting response χ_0 following the first step of the SCF cycle, as in state-of-the-art linear-response calculations, relies, by construction, upon the density (or Kohn-Sham orbitals, or density-matrix, as the case may be) not being converged to the variational ground-state for each given external parameter α. A non-optimized density of this type will typically not correspond to the ground-state for any value of α, although its subspace-total N will be. As a result, the finite-difference data points for $\alpha \neq 0$ that build the SCF linear-response χ_0 are individually not properties of the ground-states for their corresponding external potentials, noting that linear-response does not imply the sufficiency of first-order perturbation theory or first-order screening.

Put another way, the SCF χ_0 (and hence the derived U) is not a ground-state property of the unperturbed ground-state density, but instead an excited-state property (in the simple sense of non-ground-state, rather than of a resonance) dependent on the eigensystem of the non-interacting Kohn-Sham Hamiltonian. The comparison of the resulting DFT+U total-energies thus remains well defined in terms of ground-state densities, since the Kohn-Sham eigenspectra are themselves ground-state properties. However, by virtue of the SCF Hubbard U not itself being a purely ground-state density-functional property, in general, the total energies are also not necessarily so.

The precise effects of the departure from the ground-state energy surface in the calculation of SCF χ_0 have not been quantified to date, to the best of our knowledge. Therefore, while the self-consistency scheme dubbed $U^{(2)}$ seems to be optimal for use with the variational linear-response scheme, as we have shown, this result does not automatically extend to its SCF progenitor. Nonetheless, we may expect that the two inequivalent approaches for χ_0 should yield similar numerical results in practice.

VI. CONCLUSIONS

We have developed a simple, variational adaptation of the widely-used linear-response method for directly calculating the Hubbard U of DFT+U, in which the U incorporates only quantities calculated from ground-state densities. This method puts DFT+U on a first-principles footing within the context of direct-minimization DFT solvers, even the linear-scaling solvers of the type now routinely used to simulate systems which are simultaneously spatially and electronically complex[69–78]

Our formalism simplifies the analysis of parameter self-consistency schemes considerably and, at least for this specific method, there emerges a clear best choice of self-consistency criterion, $U^{(2)}$, which has been explored relatively little in the literature to date. We recommend the use of a more complicated criterion, the previously proposed $U^{(3)}$, particularly for density-non-self-consistent methods such as post-processing DFT+DMFT. In stringent calculations of the dissociated limit of the purely SIE-afflicted system PBE H_2^+, where DFT+U operates under ideal conditions, we are able to directly observe that the method corrects the SIE in the total-energy very precisely, as foreseen in Ref. 25. It does so entirely from first-principles when the $U^{(2)}$ scheme is used.

Our analysis also shows that the comparison of thermodynamically relevant DFT+U quantities such as the total-energy between dissimilar systems demanding different first-principles U parameters is, at least, well defined. This comparison evidently becomes one between purely ground-state properties, moreover, in the case where the variational linear-response method is applied together with parameter self-consistency, but there may well be other circumstances in which this also holds true. The DFT+$U_1 + U_2$ method[45], put here on a first-

principles basis, extends the DFT+$U^{(2)}$ full SIE correction of the H_2^+ total-energy to the highest occupied eigenvalue, approximately enforcing Koopman's condition.

Finally, we note that to properly account for SIE in the total-energy across the bond-length range, one would need to fully take into account the effects of subspace charge spillage, overlap and double-counting, possibly through the use of Wannier functions[81] generated self-consistently with the DFT+U electronic structure[36]. At least as important for correcting SIE in the bonding regime, perhaps, is the necessity to overcome the breakdown of the single-site approximation. For this, the account of inter-subspace SIE offered by the multi-site method DFT+U+V[67] is a promising avenue for investigation.

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