Towards a First-Principles Determination of Effective Coulomb Interactions in Correlated Electron Materials: Role of Intershell Interactions

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The determination of the effective Coulomb interactions to be used in low-energy Hamiltonians for materials with strong electronic correlations remains one of the bottlenecks for parameter-free electronic structure calculations. We propose and benchmark a scheme for determining the effective local Coulomb interactions for charge-transfer oxides and related compounds. Intershell interactions between electrons in the correlated shell and ligand orbitals are taken into account in an effective manner, leading to a reduction of the effective local interactions on the correlated shell. Our scheme resolves inconsistencies in the determination of effective interactions as obtained by standard methods for a wide range of materials, and allows for a conceptual understanding of the relation of cluster model and dynamical mean field-based electronic structure calculations.

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The behavior of electrons in the immediate proximity of the Fermi level determines most of the interesting response properties of materials with strong electronic Coulomb correlations. The *ab initio* derivation of effective Hamiltonians that capture this low-energy physics has therefore become a crucial milestone of modern condensed matter theory, and a prerequisite for materials-specific many-body calculations. While density functional techniques (DFT) [1] provide a tool for constructing the one-body part of the low-energy Hamiltonian, "downfolding" the interaction part is more subtle [2–11]. The task consists in calculating from first principles the renormalization of the Coulomb interactions when higher-energy degrees of freedom are integrated out. The constrained local density approximation (cLDA) [2–4,12] or linear response [5] schemes aim to do this implicitly by evaluating energetic differences upon particle number changes or application of perturbing fields. The more recent constrained random phase approximation identifies interaction parameters to be used in subsequent many-body calculations in a low-energy subspace as matrix elements of partially screened Coulomb interactions [13,14]. Its most important advantages over earlier schemes are probably the possibility of (1) adapting U to the chosen low-energy model and (2) assessing its full frequency dependence. For reviews, see [15–18].

The progress in calculating effective Hubbard interactions from first principles, however, also raises new questions. Here, we demonstrate that in prototypical correlated transition metal (TM) oxides and f-electron systems, standard calculations which treat only the "correlated" shell as interacting omit an important additional term, namely intershell interactions that couple the correlated shell to itinerant states, either on the same atomic site or between different atoms. Examples are d-f interactions in f-electron materials or d-ligand interactions in TM oxides. We evaluate these interactions from first principles, thus constructing a Hamiltonian that contains explicitly the d (f) orbitals and the p (spd) orbitals in TM oxides (f-electron materials) as interacting degrees of freedom. Solving this Hamiltonian in practice is a tremendous open challenge that we do not try to tackle here. In this work, we rather proceed to a further reduction of the complexity of the Hamiltonian by proposing a scheme to determine effective intrashell interactions, which are renormalized by intershell interactions. The form of this renormalization is reminiscent of an early approach dubbed "perfect screening" [4,34–36], but extends its scope to quantitative calculations by using its philosophy *within the framework of the cRPA*. Our calculations for various materials including Ce, NiO, and f-electron insulators [37] demonstrate that this "shell-folding scheme" not only fixes present problems in determining effective interactions from first principles but also gives new insight in how to treat late TM oxides within dynamical mean-field-based (DMFT) techniques [73,74].

We begin by calculating, using the cRPA implementation of [14], the interactions between TM d (or actinide f) orbitals and O $2p$ ligands to be used in a low-energy Hamiltonian treating both orbital species as correlated. For the actinide oxide UO_2 we find $U^{fp} = 1.9$ eV, as compared to an onsite f-f interaction of 6.5 eV and intersite V^{ff} of 1 eV. For NiO, $U^{dp} = 2.2$ eV still exceeds 25% of the onsite $U^{dd} = 8.6$ eV, and is larger than $V^{dd} = 1.5$ eV. These findings might explain the difficulties that DMFT-based electronic structure calculations face when dealing with late TM oxides [73–75] using a Hamiltonian without intershell interactions. Specifically, for NiO, it has been demonstrated that none of the standard double counting correction forms provide spectral properties in agreement with experiment [75]. The situation is similar for rare-earth nickelates and high-T_c cuprates where it has been argued [76] that a static treatment of intershell d-p interactions effects [77–79] may be insufficient.

Electronic structure calculations for elemental cerium usually assume a Hubbard U of the order of 5–6 eV to be applied to the f-states: DMFT calculations performed for a low-energy "f-$spdf$" Hamiltonian comprising s, p, d, and f states, and a Hubbard correction for the f states of this order of magnitude yield good agreement between theory and a vast body of experimental probes [80–87]. However, cRPA calculations for an f-$spdf$ Hamiltonian, where localized states are constructed for an energy window containing s, p, d, and f states but the polarization is constrained to only exclude screening among the f states, give a much too small value (< 1 eV) [88], moreover, in striking contrast to values of about 5 eV obtained in early atomic estimates based on the X-α approximation [89]. Even when additional screening processes are cut out, corresponding e.g., to transitions involving the Ce-t_{2g} states [88], or when the hybridization is effectively reduced by using a disentangled band structure [90], obtained U values remain on the small side.

We argue here that both considering a second shell as correlated and treating the intershell interaction at least in an effective manner—in a way reminiscent of the X-α approximation-based work—are crucial ingredients to remedy this problem. For α-Ce, assuming f and d states as correlated within cRPA, we find an intershell interaction $U^{fd} = 1.8$ eV, as compared to $U^{ff} = 6.5$ eV and a negligible intersite $V^{ff} = 0.01$ eV. The large difference in the onsite U^{ff} depending on whether a second shell is treated as correlated (and thus excluded as a screening channel in the cRPA) can be traced to the strong f-spd hybridization. Furthermore, it has been recently argued [13,15,91,92] that the effective local Hubbard interaction is a dynamical quantity. The cRPA allows for direct assessment of this frequency dependence and its consequences have been extensively studied within DMFT [92–98]. We have calculated $U(\omega)$ for Ce constructing a Hamiltonian that comprises both $4f$ and $5d$ orbitals as correlated states, denoted as "df-df" Hamiltonian, indicating that Wannier functions have been constructed for both d- and f-dominated states and both have also been cut out in the screening calculation within the cRPA formalism. The results (Fig. 1) display a striking similarity in the frequency dependence of U^{ff}, U^{fd}, and U^{dd}, and in the magnitude of U^{fd} and U^{dd}, suggesting that screening is dominated by the same screening processes (e.g., transitions from f or d states to sp-dominated states via strong hybridization as well as plasmonlike excitations). Consequently, the differences $\tilde{U}^{ff/dd} = U^{ff/dd} - U^{fd}$ are only weakly frequency-dependent quantities. Below, we argue that these differences acquire a physical meaning as effective interactions when intershell interactions are taken into account in an effective manner.

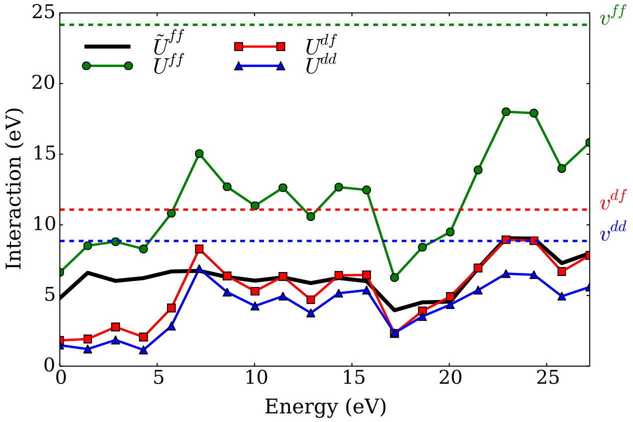

FIG. 1. $U(\omega)$ for df-df and effective (SF) Hamiltonians for cerium. For U^{ff} and U^{dd} the monopole term F^0 is plotted and for U^{df} we give an orbital average.

Consider a multiorbital Hubbard Hamiltonian for materials where two different orbital shells are treated as correlated. Since, besides Ce, important examples are provided by the TM d and ligand p states in TM compounds, we will refer to these two shells as d and p shells, with the respective "correlated" and "ligand" subspaces denoted by $\mathcal{C}$ and $\mathcal{L}$. Our basic assumption is that DFT, within the local density (LDA) or generalized gradient approximation, gives a good estimate for the total energy as a function of the expectation values of the number operators N_d and N_p of the two shells. We further assume that we know the intra- and intershell interactions U^{dd}, U^{pp}, and U^{dp}. In practice, we obtain those from the standard cRPA by suppressing *all* screening channels within the full $\mathcal{C} + \mathcal{L}$ space. Following the spirit of "LDA++" [99,100], we then define a *bare* one-body Hamiltonian H_0 as the LDA estimate from which average interactions within the d and p shells have been subtracted. Our multiorbital Hubbard Hamiltonian now reads $H = H_0 + H_{\mathrm{int}} - \mu N_{\mathrm{tot}}$, where $H_{\mathrm{int}} = \sum_{\mathbf{R}} h_{\mathbf{R}}$ becomes a sum over the positions $\mathbf{R}$ of the atoms carrying the correlated shell:

$$h_{\mathbf{R}} = \frac{1}{2} \sum_{\substack{(m\sigma)\neq(m'\sigma') \\ m,m'\in\mathcal{C}}} U^{dd}_{m\sigma m'\sigma'} n_{m\sigma} n_{m'\sigma'} + \frac{1}{2} \sum_{\substack{(m\sigma)\neq(m'\sigma') \\ m,m'\in\mathcal{L}}} U^{pp}_{m\sigma m'\sigma'} n_{m\sigma} n_{m'\sigma'} + \sum_{\sigma,\sigma'} U^{dp} N_{d\sigma} N_{p\sigma'}. \tag{1}$$

Here, $U^{dd}_{m\sigma m'\sigma'}$ and $U^{pp}_{m\sigma m'\sigma'}$ are the spin- and orbital-resolved interaction matrix elements, $N_{(d/p)\sigma} = \sum_{m\in\mathcal{C}/\mathcal{L}} n_{m\sigma}$ and $n_{m\sigma} = c^{\dagger}_{m\sigma} c_{m\sigma}$. To simplify the notation, we have omitted the $\mathbf{R}$ indices on the operators, and the intershell interactions couple only to the total charge on a given shell. A purely algebraic manipulation allows us to rewrite this Hamiltonian as

$$h_{\mathbf{R}} = \frac{1}{2} \sum_{\substack{(m\sigma)\neq(m'\sigma') \\ m,m' \in \mathcal{C}}} \tilde{U}^{dd}_{m\sigma m'\sigma'} n_{m\sigma} n_{m'\sigma'} + \frac{1}{2} \sum_{\substack{(m\sigma)\neq(m'\sigma') \\ m,m' \in \mathcal{L}}} \tilde{U}^{pp}_{m\sigma m'\sigma'} n_{m\sigma} n_{m'\sigma'} + \frac{U^{dp}}{2} N(N-1), \tag{2}$$

with $N = \sum_{\sigma}(N_{d\sigma} + N_{p\sigma})$ and $\tilde{U}_{m\sigma m'\sigma'} = U_{m\sigma m'\sigma'} - U^{dp}$.

The key observation here is that a Hamiltonian with explicit intershell interactions can be rewritten as a sum of interacting Hamiltonians for the two shells, coupled only through an interaction acting on the total charge. The calculations further simplify if the interactions on the p-shell can be neglected. The usual argument consists in invoking the nearly complete filling of this shell, which impedes charge fluctuations and allows replacement of operators n_p by their static mean-field values $\langle n_p \rangle$, but this is difficult to justify in late TM oxides where d-p fluctuations are generally the most efficient screening mechanism, substantially reducing the p occupations. However, as we will see below, U^{dp} can be comparable in magnitude to the intraligand-shell interactions U^{pp}, making the effective interaction $\tilde{U}^{pp} = U^{pp} - U^{dp}$ small. The Hamiltonian then has a $d - dp$ form, with correlated d and noncorrelated p electrons, and contains the renormalization of the dd interactions by the intershell interactions: $\tilde{U}^{dd} = U^{dd} - U^{dp}$. Analogously to "downfolding" in energy space, we refer to this scheme as "shell folding" (SF).

While very suggestive in the sense of the above interpretation, Eq. (2) involves a certain number of subtleties. First, we have divided the solid into cells centered on atoms carrying correlated shells, and constructed ligand Wannier functions *centered on these correlated atoms*. For the prototypical material NiO, this construction is explicitly discussed in the Supplemental Material [101]. It is similar to what is routinely done in cluster model calculations, where hybridizing cluster ligand orbitals are combinations of neighboring ligand orbitals that are able, by symmetry considerations, to couple to the correlated orbitals. Akin to a Zhang-Rice-type construction [105], a unitary transformation rotates the original Hamiltonian in ligand-centered p orbitals basis into a "cell Hamiltonian" expressed in TM-centered ligand Wannier functions. The above p degrees of freedom are to be understood in this sense [106]. We stress that when rotated back into the usual atom-centred basis, the resulting Hamiltonian would contain explicit intershell interactions. Furthermore, we have implicitly assumed that the total particle number *on a given cell* is a conserved quantity: the dominant screening channels involve the immediate neighbor ligands, while long-range processes within the dp subspace are neglected. This is a generalization of the assumption of "perfect screening" discussed for transition metals [34], namely that any change in the number of d electrons is compensated by an opposite change in the number of sp electrons. Integrating this philosophy into the cRPA framework, as we do here, allows us to take into account screening by other degrees of freedom in addition to the ones mediated by the U^{dp} interactions and thus to extend the scope of the scheme to a quantitative description.

The exact rewriting of the Hamiltonian can be understood in a complementary manner, which moreover allows us to assess the limits of perfect screening: one can formulate the problem as the quest for an optimal auxiliary system with decoupled correlated shells reproducing the free energy of the full system as closely as possible. Consider the auxiliary Hamiltonian:

$$\tilde{h}_{\mathbf{R}} = \frac{\tilde{U}^{dd}}{2} \sum_{\substack{(m\sigma)\neq(m'\sigma') \\ m,m' \in \mathcal{C}}} n_{m\sigma} n_{m'\sigma'} + \frac{\tilde{U}^{pp}}{2} \sum_{\substack{(m\sigma)\neq(m'\sigma') \\ m,m' \in \mathcal{L}}} n_{m\sigma} n_{m'\sigma'}.$$

According to the Peierls-Feynman-Bogoliubov variational principle, the optimal value of the (for simplicity, spherically and spin- averaged) interactions $\tilde{U}^{dd}$ and $\tilde{U}^{pp}$ are those that minimize the auxiliary free energy $\tilde{F} = F[\tilde{h}_{\mathbf{R}}] + \langle h_{\mathbf{R}} - \tilde{h}_{\mathbf{R}} \rangle_0$, where $\langle \cdots \rangle_0$ refers to the average taken with the auxiliary Hamiltonian, and $h_{\mathbf{R}}$ is given by Eq. (1). From the stationarity condition $\partial \tilde{F} / \partial \tilde{U}^{dd} = 0$ we obtain

$$\tilde{U}^{dd} = U^{dd} + \frac{2U^{dp}D^{dp} + (U^{pp} - \tilde{U}^{pp})D^{pp}}{D^{dd}}, \tag{3}$$

where (for $X, Y = d$ or p)

$$D^{XY} = \frac{\partial}{\partial \tilde{U}^{dd}} \sum_{(i\sigma)\neq(j\sigma')} \langle n^X_{i\sigma} n^Y_{j\sigma'} \rangle_0, \tag{4}$$

and an analogous equation for $\tilde{U}^{pp}$. The optimal interactions are the solutions of this system of equations. If, in addition, we assume that $N = N_d + N_p$ is invariant with respect to changes in $\tilde{U}^{dd/pp}$, these solutions simplify to $\tilde{U}^{dd} = U^{dd} - U^{dp}$ and $\tilde{U}^{pp} = U^{pp} - U^{dp}$, in agreement with Eq. (2). This imposes that charge may be displaced from the correlated site to the ligand orbitals within the cluster as a result of changes in the interaction, which is equivalent to our assumption that screening takes dominantly place within the immediate neighborhood of a given atom. Imposing the requirement that increasing the interaction strength only results in charge flow from a site to its nearest neighbors in the single-orbital extended Hubbard model (that is, in an effective Hamiltonian with local and intersite interactions), gives rise to an analogous result as derived in Ref. [108]. In this case the effective interaction becomes $\tilde{U} = U - V_{nn}$, where V_{nn} is the nearest-neighbor interaction. Here, a multiorbital model with two correlated shells and intershell interactions is mapped onto a model with reduced intrashell interactions only and a coupling only to the total charge on a cell, or if $U^{pp} - U^{dp}$ can also be neglected, onto a model with only one correlated shell.

We now discuss how the above shell-folding scheme resolves contradictions arising in modeling specific

TABLE I. Slater integrals F^k for correlated shells, average intraorbital U^{pp} for ligand p shells and intershell $U^{dp/fp}$ for (a) Ce for f-$spdf$, df-df, $spdf$-$spdf$, and (b) NiO and actinide oxides for d-dp, dp-dp, f-fp, fp-fp, and SF models as appropriate. All values in eV.

Ce	f-$spdf$	df-df			$spdf$-$spdf$			
		f-f	d-d	SF	ff	d-d	p-p	s-s
F^0	0.9	6.5	1.5	**4.7**	7.9	1.8	1.0	0.9
F^2	5.8	8.8	2.7	**8.8**	9.4	3.1	3.8	
F^4	5.6	6.4	2.5	**6.4**	6.5	2.6		
F^6	4.7	5.1		**5.1**	5.1			
U^{fd}		1.8			2.4			

	NiO			UO_2				PuO_2	CmO_2
	d-dp	dp-dp	SF	f-f	f-fp	fp-fp	SF	SF	SF
F^0	6.1	8.6	**6.4**	3.5	3.9	6.5	**4.6**	**5.3**	**5.9**
F^2	9.7	10.1	**10.1**	5.3	5.8	6.2	**6.2**	**7.3**	**8.1**
F^4	6.6	6.8	**6.8**	4.3	4.9	5.0	**5.0**	**5.6**	**6.1**
F^6				3.9	4.1	4.2	**4.2**	**4.4**	**4.8**
U^{pp}		6.8	**4.6**			6.0	**4.1**	**4.3**	**4.6**
$U^{dp/fp}$		2.2				1.9		(2.0)	(2.1)

materials. In practice we write the intrashell interactions using the Slater integrals F^k, such that the renormalization is done for the monopole F^0 term. For α-Ce, our SF scheme finds $F^0_{ff} = 4.7$ eV. More interestingly, the intrashell interactions $F^0_{dd} = 1.5$ eV for the d orbitals are renormalized by the same mechanism to approximately zero since the intershell interaction equals the average intraorbital d-d interaction within numerical accuracy; see Fig. 1 at $\omega = 0$. This justifies the construction of the Hamiltonian for DMFT calculations for cerium, and in particular the fact that only f states are treated as correlated. Furthermore, these effective parameters are in better agreement with the $U \sim 5$–6 eV needed in practice than those obtained naively within the cRPA.

We now turn to the case of the correlated insulators NiO and actinide oxides in their paramagnetic phases. The interaction parameters calculated for a Hamiltonian including explicitly the three kinds of interactions (dd, dp, pp) (or ff, fp, pp for the actinide compounds) are given in Table I. Conceptually speaking, one could directly use those in a calculation treating all these interactions by many-body methods. In practice, this is too computationally heavy, and the reduction by shell folding is particularly interesting. Also here, the F^0 for the correlated d subspace in the SF Hamiltonian (see Table I) is found to be larger than that calculated within a d-dp setup. Extensive cluster model calculations exist for this compound, where interaction strengths have been adjusted so as to reproduce experimental spectra. These optimal values coincide with our calculations within numerical accuracy: Ref. [109] uses $F^0 = 6.5$ eV and finds excellent agreement with experiment (see Fig. 3 in Ref. [109]). In contrast to Ce, however,

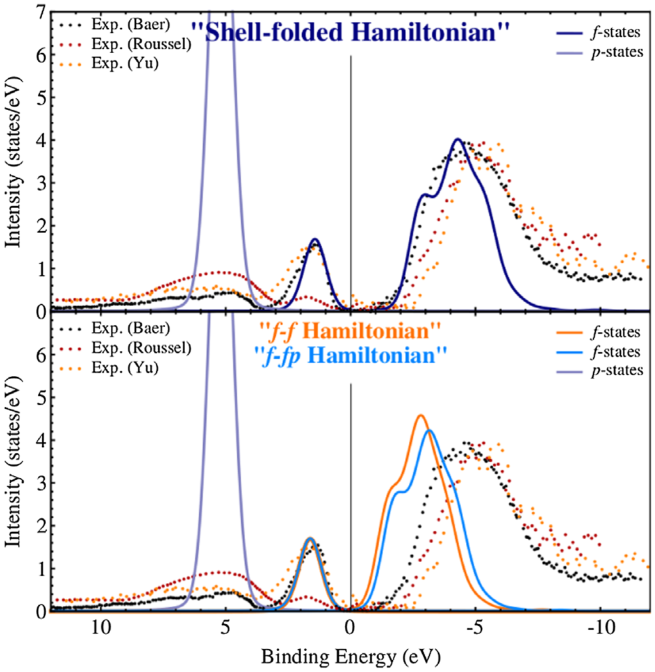

FIG. 2. PES and IPES spectra for UO_2 using interaction parameters obtained in the f-f, f-fp, and SF models compared to experimental spectra [111–113].

the effective value for the "uncorrelated" orbitals ($U^{pp} = 4.6$ eV) is non-negligible. This is in agreement with typical values of U^{pp} measured by Auger spectroscopy in transition metal oxides (see e.g. [110]). For practical reasons, one might still have to drop the effective U^{pp} interactions, relying on the low concentration of holes in the p-manifold to make this approximation reasonable.

The fluorite structure actinide oxides UO_2, PuO_2, and CmO_2 are insulating f-electron compounds that we consider in their non- or paramagnetic phases. In particular, UO_2 has received much interest given its role as a nuclear fuel, and its electronic structure has been studied extensively [114–118]. We have calculated the interactions corresponding to f-f, f-fp, and fp-fp Hamiltonians for UO_2. The Slater integrals F^k needed to parametrize these interactions are given in Table I. The increased localization of the f orbitals in the f-fp model relative to the f-f model is reflected in the larger values of F^k. The magnitude of f-f interactions in UO_2 is significantly larger in the fp-fp model, signaling the importance of p-to-f screening transitions. While integration of the intershell interactions reduces U^{ff} to the SF value of 4.6 eV, this value remains larger than that obtained in the f-only models. As we proceed along the actinide series, the value of U^{ff} in the f-fp model decreases from 3.9 (UO_2) to 3.5 (PuO_2) to 3.4 eV (CmO_2). The increased screening efficiency of the O $2p$ states as the charge-transfer gap shrinks outweighs the decreased f-orbital extension as the nuclear charge increases. In contrast, the SF $\tilde{U}^{ff}$ increases from 4.6 (UO_2) to 5.3 (PuO_2) to 5.9 eV (CmO_2). In this case, transitions between p and f states do not contribute to the polarization, and the increased localization of $5f$ states determines the overall trend. For UO_2, the p-f charge-transfer energy calculated from the local part of the DFT Hamiltonian, $\Delta = 5.2$ eV, is larger than the $\tilde{U}^{ff} = 4.6$ eV indicating the Mott-Hubbard character of the gap in UO_2 (opening between f-dominated states). On the other hand, PuO_2 and CmO_2, which respectively have $\Delta = 4.2$ and 3.4 eV, are found to be charge-transfer insulators, with a gap between f and p states, in agreement with Ref. [117]. With our cRPA results we have performed simulations of (inverse-)photoemission experiments using a configuration-interaction cluster model [132,133] for UO_2 [134]. The spectra obtained using parameters from the f-f, f-fp, and shell-folded models are compared to experiments in Fig. 2. The gap between the PES and IPES peaks is largely determined by U^{ff} (given the classification of UO_2 as a Mott-Hubbard insulator) and is therefore sensitive to the value of F^0. Clearly, the calculations both within the f-f and f-fp Hamiltonians severely underestimate the gap. The SF model $\tilde{U}^{ff}$ matches the experimental estimate of 4.6 ± 0.8 eV to numerical precision [111] and yields spectra in excellent agreement with experiments [135].

In summary, we have presented a scheme for first-principles determination of effective Coulomb interactions for materials where ligand-to-correlated-shell hybridizations and interactions cannot be neglected. In the simplest version, intrashell interactions are reduced by the intershell ones, and this estimate provides a remarkably good description of our test materials. Our scheme cures ambiguities in current cRPA calculations in the case of entangled band structures. Finally, our work builds a connection between cluster model calculations, highly successful for spectroscopies of strongly correlated late TM oxides, and techniques such as DMFT and its extensions treating the solid by embedding an effective local problem into an auxiliary bath.

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