Supplemental Material:
Ab initio Full Cell *GW*+DMFT for Correlated Materials

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I. BATH DISCRETIZATION ALGORITHM

In order to use a wavefunction-based solver, the hybridization $\boldsymbol{\Delta}(\omega)$ in our full cell *GW*+DMFT approach is represented by a finite set of discrete bath sites and couplings. We first start with a direct discretization of $\boldsymbol{\Delta}(\omega)$ on the real axis. We consider $\boldsymbol{\Delta}(\omega)$ as the Hilbert transform [1]

$$\boldsymbol{\Delta}(\omega) = \int \frac{\mathbf{J}(\epsilon)}{\omega - \epsilon} d\epsilon \qquad (1)$$

with the spectral density

$$\mathbf{J}(\epsilon) = -\frac{1}{\pi} \mathbf{Im}\boldsymbol{\Delta}(\epsilon + i\eta), \qquad (2)$$

where η is a broadening parameter. The Hilbert transform integral can be approximated by a numerical quadrature (Gauss-Legendre in this work) along the real axis

$$\boldsymbol{\Delta}(\omega) = \sum_{n=1}^{N_\omega} w_n \frac{\mathbf{J}(\epsilon_n)}{\omega - \epsilon_n}, \qquad (3)$$

where w_n and ϵ_n are the weights and positions of the N_ω quadrature grid points. To derive the couplings between the impurity and bath sites, we diagonalize the spectral density

$$\mathbf{J}(\epsilon_n) = \mathbf{U}^{(n)} \lambda^{(n)} \mathbf{U}^{(n)\dagger}. \qquad (4)$$

Eq. 3 then becomes:

$$\Delta_{ij}(\omega) = \sum_{n=1}^{N_\omega} \sum_{k=1}^{N_C} \frac{V_{ik}^{(n)} V_{jk}^{(n)}}{\omega - \epsilon_n}, \qquad (5)$$

with

$$V_{ik}^{(n)} = w_n^{\frac{1}{2}} U_{ik}^{(n)} (\lambda_{kk}^{(n)})^{\frac{1}{2}}, \qquad (6)$$

where N_C is the number of impurity orbitals. Thus, $V_{ik}^{(n)}$ and ϵ_n can be interpreted as the impurity-bath couplings and energy levels of bath orbitals.

In this direct discretization within the full cell approach, the number of bath orbitals is formally $N_b = N_\omega N_C$, which can easily be as many as a few hundred, as N_C includes all orbitals in the unit cell. To reduce the bath size and thus computational cost, we only couple bath orbitals to the IAOs (valence

orbitals). Note that PAOs (non-valence virtuals) are still included in the embedding problem and interact with the IAOs. With this choice, the number of bath orbitals is reduced to $N_b = N_\omega N_{\mathrm{IAO}}$. Moreover, we remove the bath orbitals which are very weakly coupled to the impurity. As seen in Eq. 6, the scale of the bath coupling is set by the eigenvalues $\lambda_{kk}^{(n)}$. By dropping the bath orbitals with eigenvalues below a threshold, we can further decrease the bath dimension.

However, using the bath parameters derived this way, we find that the *GW*+DMFT self-energies may be non-causal, i.e., the imaginary part of $\boldsymbol{\Sigma}(\mathbf{k}, \omega)$ may not be always negative:

$$\boldsymbol{\Sigma}(\mathbf{k}, \omega) = \boldsymbol{\Sigma}^{GW}(\mathbf{k}, \omega) + \boldsymbol{\Sigma}_{\mathrm{imp}}(\omega) - \boldsymbol{\Sigma}_{\mathrm{DC}}^{GW}(\omega). \qquad (7)$$

This indicates that the bath parameters do not approximate the hybridization well, leading to inaccurate relative self-energy magnitudes between the impurity self-energy $\boldsymbol{\Sigma}_{\mathrm{imp}}(\omega)$ and the $G_0 W_0$ double-counting self-energy $\boldsymbol{\Sigma}_{\mathrm{DC}}^{GW}(\omega)$.

Therefore, we further optimize the bath parameters $\{V_{ip}^{(n)}, \epsilon_n\}$ with the initial guess obtained from Eqs. 5 and 6, to minimize a cost function over a range of real-frequency points $\{\omega_l\}$:

$$D = \sum_{\omega_l} \sum_{ij} \left(\Delta_{ij}(\omega_l + i\eta) - \sum_{n=1}^{N_\epsilon} \sum_{p=1}^{N_p} \frac{V_{ip}^{(n)} V_{jp}^{(n)}}{\omega_l + i\eta - \epsilon_n} \right)^2, \qquad (8)$$

We used a trust region reflective algorithm [2] (with bounds on bath energies) as implemented in SciPy to perform this least-square optimization.

In this study, we used 8×16 (16 bath energies and 8 bath orbitals on each bath energy level) bath orbitals for Si, 9×8 bath orbitals for NiO, 8×6 bath orbitals for α-Fe_2O_3 and 9×13 bath orbitals for $SrMoO_3$. The broadening factor η is set to 0.1 a.u. for Si, NiO and α-Fe_2O_3, and 0.02 a.u. for $SrMoO_3$.

II. BATH DISCRETIZATION ERROR

The smallest bath number we used in this work is for α-Fe_2O_3 (48 bath orbitals), due to the large impurity size (124 impurity orbitals). Therefore, we present a numerical test here to investigate how sensitive our results are with respect to the finite bath discretization. We used a series of numbers of bath orbitals (32, 40, 48, 56, 64, 80) and two broadenings (0.1 a.u. and 0.05 a.u.) for the bath discretization. Because of the high computational cost when using more than 48 bath orbitals, here we only perform a one-shot full cell *GW*+DMFT calculation based the $G_0 W_0$@PEB0 hybridization.
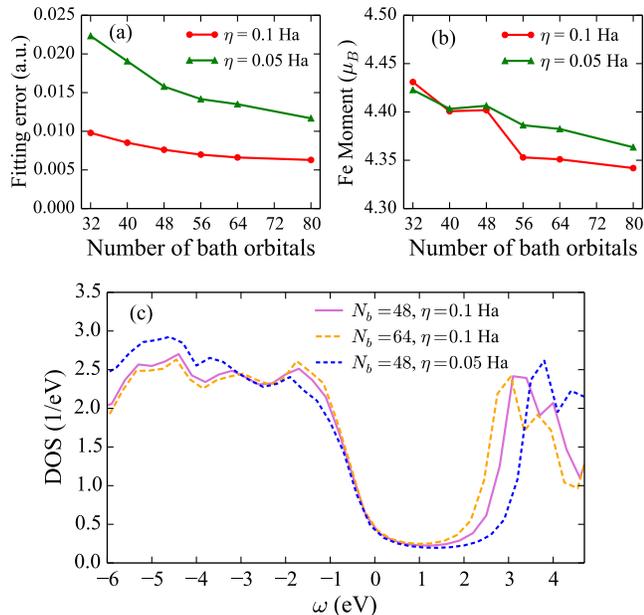
FIG. 1. Numerical test on *GW*+DMFT bath discretization errors for α-Fe₂O₃. (a) Bath fitting error defined in Eq. 9. (b) Fe magnetic moment with respect to the number of bath orbitals and broadening factor. (c) Local *GW*+DMFT DOS for different bath numbers and broadenings.

We define the bath fitting error per matrix element on each

fitting frequency as:

$$\delta = \frac{1}{N_{\mathrm{IAO}}} \sqrt{\frac{D}{N_{\omega_l}}}, \qquad (9)$$

where N_{IAO} is the number of IAO orbitals (corresponding to the dimension of the hybridization matrix) and N_{ω_l} is the number of frequency points we choose to optimize the cost function on. In this case, $N_{\mathrm{IAO}} = 48$ and $N_{\omega_l} = 15$.

We first plot the *GW*+DMFT bath fitting error in Fig. 1(a). As the number of bath orbitals grows, the bath fitting errors go down. It is also clear that a smaller broadening $\eta = 0.05$ a.u. makes it harder to fit the hybridization. We then investigate how the other *GW*+DMFT results are influenced by the bath discretization error. It is shown in Fig. 1(b) that the Fe magnetic moment is barely affected. The Fe magnetic moment computed using 48 bath orbitals and 0.1 a.u. broadening is shown to be within 0.05 μ_B compared to the moment computed using 80 bath orbitals and 0.05 a.u. broadening. In Fig. 1, we further show the local density of states (DOS) computed using different bath discretization parameters. We find that the spectral shape is not affected much by the bath discretization parameters. The band gap computed using 48 bath orbitals and 0.1 a.u. broadening is about 0.2 eV larger than the gap computed using 64 bath orbitals and 0.1 a.u. broadening, and 0.4 eV smaller than the gap computed using 48 bath orbitals and 0.05 a.u. broadening. Therefore, we conclude that it is likely that the *GW*+DMFT band gap error for α-Fe₂O₃ due to the finite bath discretization is within 0.4 eV.

[1] I. de Vega, U. Schollwöck, and F. A. Wolf, Phys. Rev. B 92, 155126 (2015).

[2] M. A. Branch, T. F. Coleman, and Y. Li, SIAM J. Sci. Comput. 21, 1 (1999).