Supplementary Information for Quantum simulations of materials on near-term quantum computers

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1 Derivation of the embedding formalism

Within density functional theory (DFT), the single-particle electronic structure of a physical system is determined by the Kohn-Sham (KS) equation

$$H^{\mathrm{KS}} \left|\psi_m\right\rangle = \varepsilon_m \left|\psi_m\right\rangle, \tag{1}$$

where the Kohn-Sham Hamiltonian $H^{\mathrm{KS}} = T + V_{\mathrm{ion}} + V_{\mathrm{H}} + V_{\mathrm{xc}}$ includes the kinetic operator as well as ionic, Hartree and exchange-correlation potentials; ε_m and ψ_m are eigenvalues and eigenvectors of H^{KS}. The density response function of the Kohn-Sham system is

$$\chi_0(\boldsymbol{x}_1, \boldsymbol{x}_2) = 2\sum_{i<j}(f_i - f_j)\frac{\langle\psi_i|\hat{n}(\boldsymbol{x}_1)|\psi_j\rangle\,\langle\psi_j|\hat{n}(\boldsymbol{x}_2)|\psi_i\rangle}{\varepsilon_i - \varepsilon_j} \tag{2}$$

where $\hat{n}(\boldsymbol{x})$ is the density operator at $\boldsymbol{x} = \boldsymbol{r}\sigma$ and $\boldsymbol{r}$ and σ are coordinate and spin indeces, respectively, f_i denotes the occupation number of the spin orbital i (not to be confused with the Hartree-exchange-correlation kernel f used in the main text).

The set of Kohn-Sham orbitals constitutes a complete orthogonal basis of the one-particle Hilbert space. In this work we define an active space (denoted as A) as a subset of the orthogonal basis where relevant electronic excitations take place. We note that such a definition is closely related to the notion of active spaces in multireference quantum chemistry methods, in the sense that it is a set of single-particle orbitals among which all possible excitations are explicitly taken into account; however, in the embedding theory developed here, the environmental effects manifest as a renormalization of one-body and two-body terms in the Hamiltonian, and we do not keep track of wavefunctions in the environment after effective Hamiltonians are constructed.

For a given definition of A, χ_0 can be partitioned into two parts:

$$\chi_0(\boldsymbol{x}_1, \boldsymbol{x}_2) = \chi_0^{\mathrm{A}}(\boldsymbol{x}_1, \boldsymbol{x}_2) + \chi_0^{\mathrm{E}}(\boldsymbol{x}_1, \boldsymbol{x}_2) \tag{3}$$

$$\chi_0^{\mathrm{A}}(\boldsymbol{x}_1, \boldsymbol{x}_2) = 2\sum_{i\in\mathrm{A}}\sum_{\substack{j>i\\ j\in\mathrm{A}}}(f_i - f_j)\frac{\langle\psi_i|\hat{n}(\boldsymbol{x}_1)|\psi_j\rangle\,\langle\psi_j|\hat{n}(\boldsymbol{x}_2)|\psi_i\rangle}{\varepsilon_i - \varepsilon_j} \tag{4}$$

$$\begin{aligned}\chi_0^{\mathrm{E}}(\boldsymbol{x}_1, \boldsymbol{x}_2) = {} & 2\sum_{i\in\mathrm{A}}\sum_{\substack{j>i\\ j\notin\mathrm{A}}}(f_i - f_j)\frac{\langle\psi_i|\hat{n}(\boldsymbol{x}_1)|\psi_j\rangle\,\langle\psi_j|\hat{n}(\boldsymbol{x}_2)|\psi_i\rangle}{\varepsilon_i - \varepsilon_j}\\ & +2\sum_{i\notin\mathrm{A}}\sum_{\substack{j>i\\ j\in\mathrm{A}}}(f_i - f_j)\frac{\langle\psi_i|\hat{n}(\boldsymbol{x}_1)|\psi_j\rangle\,\langle\psi_j|\hat{n}(\boldsymbol{x}_2)|\psi_i\rangle}{\varepsilon_i - \varepsilon_j}\\ & +2\sum_{i\notin\mathrm{A}}\sum_{\substack{j>i\\ j\notin\mathrm{A}}}(f_i - f_j)\frac{\langle\psi_i|\hat{n}(\boldsymbol{x}_1)|\psi_j\rangle\,\langle\psi_j|\hat{n}(\boldsymbol{x}_2)|\psi_i\rangle}{\varepsilon_i - \varepsilon_j}\end{aligned} \tag{5}$$

where the superscript E denotes the environment of the active space.

Within the RPA, one can define the partial screened Coulomb interaction $W^{\mathrm{E}}_{\mathrm{RPA}}$ as

$$W^{\mathrm{E}}_{\mathrm{RPA}} = V + V\chi_0^{\mathrm{E}}W^{\mathrm{E}}_{\mathrm{RPA}} \tag{6}$$

where V represents the bare Coulomb interaction. In the cRPA formalism, $W^{\mathrm{E}}_{\mathrm{RPA}}$ is used as effective electron interactions in A, and has the property that the full RPA screened Coulomb interaction W_{RPA} can be obtained by further screening $W^{\mathrm{E}}_{\mathrm{RPA}}$ with χ_0^{A}

$$W_{\mathrm{RPA}} = W^{\mathrm{E}}_{\mathrm{RPA}} + W^{\mathrm{E}}_{\mathrm{RPA}}\chi_0^{\mathrm{A}}W_{\mathrm{RPA}} \tag{7}$$

To derive a formalism that goes beyond the RPA and includes exchange-correlation interactions between electrons, we consider a system subject to a perturbative potential $\delta V_{\rm bare}$. The corresponding screened potential is denoted as $\delta V_{\rm scf}$. We define self-consistent and bare charge density responses as

$$\delta n_{\rm scf} = \chi \delta V_{\rm bare} = \chi_0 \delta V_{\rm scf} \tag{8}$$

$$\delta n_{\rm bare} = \chi_0 \delta V_{\rm bare} \tag{9}$$

In the presence of a perturbation, the Hartree-exchange-correlation potential of the system changes by $\delta V_{\rm Hxc} = f \delta n_{\rm scf}$, where $f = \frac{\delta V_{\rm Hxc}}{\delta n_{\rm scf}} = V + f_{\rm xc}$ is the Hartree-exchange-correlation kernel introduced in the main text.

The functional derivative of $\delta V_{\rm Hxc}$ with respect to $\delta n_{\rm bare}$ is equal to the screened Coulomb interaction W

$$W = \frac{\delta V_{\rm Hxc}}{\delta n_{\rm bare}} = f + f\chi f \tag{10}$$

We note that W defined above represents the interaction between electrons in the system (i.e. it is the electron-electron screened Coulomb interaction) and is widely used in first-principles theories of electron-phonon coupling [1, 2]. W should not be confused with test-charge test-charge screened Coulomb interaction $W_{\rm TC-TC}$ or electron-test-charge screened Coulomb interaction $W_{\rm E-TC}$ [3, 4]. W, $W_{\rm TC-TC}$, and $W_{\rm E-TC}$ all reduce to $W_{\rm RPA}$ when $f_{\rm xc} = 0$, but represent different types of screened Coulomb interactions beyond the RPA.

From Eq. 10, $\delta V_{\rm Hxc}$ can be written as

$$\begin{aligned}
\delta V_{\rm Hxc} &= W \delta n_{\rm bare} \\
&= f \delta n_{\rm bare} + f\chi_0 W \delta n_{\rm bare} \\
&= \left(\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \right) \delta n_{\rm bare} + \left(\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \right) \chi_0 W \delta n_{\rm bare} \\
&= \left(\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \right) \delta n_{\rm bare} + \left(\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \right) \delta n_{\rm scr}
\end{aligned} \tag{11}$$

where we defined the screening density

$$\delta n_{\rm scr} = \chi_0 W \delta n_{\rm bare} = \chi f \delta n_{\rm bare} \tag{12}$$

and the self-consistent charge density response is simply the sum of bare and screening contributions:

$$\delta n_{\rm scf} = \delta n_{\rm bare} + \delta n_{\rm scr} \tag{13}$$

Now we consider a bare change of density in the A space, denoted by $\delta n^{\rm A}_{\rm bare}$, and we consider a constrained screening process that only occurs in the E space, characterized by $\chi_0^{\rm E} = \frac{\delta n^{\rm E}_{\rm scf}}{\delta V_{\rm scf}}$. The resulting screening density $\delta n_{\rm scr}$ thus belongs to the E space, and we denote it by

$$\delta n^{\rm E}_{\rm scr} = \chi^{\rm E} f \delta n^{\rm A}_{\rm bare} \tag{14}$$

where $\chi^{\rm E}$ is defined as

$$\chi^{\rm E} = \chi_0^{\rm E} + \chi_0^{\rm E} f \chi^{\rm E} \tag{15}$$

The resulting change of the Hartree-exchange-correlation potential, denoted by $\delta V^{\rm c}_{\rm Hxc}$ (c stands for constrained, indicating the fact that screening processes in A are not included), is given by:

$$\begin{aligned}
\delta V^{\rm c}_{\rm Hxc} &= \left(\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \right) \delta n^{\rm A}_{\rm bare} + \left(\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \right) \delta n^{\rm E}_{\rm scr} \\
&= \left[\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} \delta n^{\rm A}_{\rm bare} + \left(\frac{\delta V_{\rm H}}{\delta n_{\rm scf}} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \right) \delta n^{\rm E}_{\rm scr} \right] + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \delta n^{\rm A}_{\rm bare} \\
&= \frac{\delta V^{\rm eff}_{\rm H}}{\delta n_{\rm scf}} \delta n^{\rm A}_{\rm bare} + \frac{\delta V_{\rm xc}}{\delta n_{\rm scf}} \delta n^{\rm A}_{\rm bare}
\end{aligned} \tag{16}$$

where we grouped terms in the square bracket and formally defined:

$$\frac{\delta V_{\mathrm{H}}^{\mathrm{eff}}}{\delta n_{\mathrm{scf}}} = \frac{\delta V_{\mathrm{H}}}{\delta n_{\mathrm{scf}}} + \left(\frac{\delta V_{\mathrm{H}}}{\delta n_{\mathrm{scf}}} + \frac{\delta V_{\mathrm{xc}}}{\delta n_{\mathrm{scf}}} \right) \frac{\delta n_{\mathrm{scr}}^{\mathrm{E}}}{\delta n_{\mathrm{bare}}^{\mathrm{A}}} \tag{17}$$

Recall that $f = \frac{\delta V_{\mathrm{Hxc}}}{\delta n_{\mathrm{scf}}}$. Thus, for a general change of density δn_{scf}, the resulting change of the Hartree-exchange-correlation potential is

$$\delta V_{\mathrm{Hxc}} = \frac{\delta V_{\mathrm{H}}}{\delta n_{\mathrm{scf}}} \delta n_{\mathrm{scf}} + \frac{\delta V_{\mathrm{xc}}}{\delta n_{\mathrm{scf}}} \delta n_{\mathrm{scf}} \tag{18}$$

By comparing Eq. 16 with Eq. 18, we see that the constrained change of Hartree-exchange-correlation potential $\delta V_{\mathrm{Hxc}}^{\mathrm{c}}$ induced by $\delta n_{\mathrm{bare}}^{\mathrm{A}}$ is equivalent to the unconstrained change of Hartree-exchange-correlation potential δV_{Hxc} induced by δn_{scf} in a system with effective electron-electron interaction:

$$\begin{aligned} V^{\mathrm{eff}} &= \frac{\delta V_{\mathrm{H}}^{\mathrm{eff}}}{\delta n_{\mathrm{scf}}} = \frac{\delta V_{\mathrm{H}}}{\delta n_{\mathrm{scf}}} + \left(\frac{\delta V_{\mathrm{H}}}{\delta n_{\mathrm{scf}}} + \frac{\delta V_{\mathrm{xc}}}{\delta n_{\mathrm{scf}}} \right) \frac{\delta n_{\mathrm{scr}}^{\mathrm{E}}}{\delta n_{\mathrm{bare}}^{\mathrm{A}}} \\ &= V + f \chi^{\mathrm{E}} f \end{aligned} \tag{19}$$

We represent χ^{E}, f and other relevant quantities on a compact basis obtained through a low-rank decomposition of the dielectric matrix [59, 60] obtained using density functional perturbation theory [5] (see also [6, 7, 8], and references therein), and evaluate f_{xc} with a finite-field algorithm [61, 62].

After V^{eff} is obtained, the effective one-particle term t_{ij}^{eff} is computed from the Kohn-Sham Hamiltonian by subtracting a double-counting term [63] computed at the Hartree-Fock level

$$t_{ij}^{\mathrm{eff}} = H_{ij}^{\mathrm{KS}} - \left(\sum_{kl} V_{ikjl}^{\mathrm{eff}} \rho_{kl} - \sum_{kl} V_{ijkl}^{\mathrm{eff}} \rho_{kl} \right) \tag{20}$$

where ρ is the one-electron density matrix.

We note that throughout this work we used the following index notation for V:

$$V_{ijkl} = \int d\boldsymbol{x}_1 d\boldsymbol{x}_2 \frac{\varphi_i^*(\boldsymbol{x}_1) \varphi_j^*(\boldsymbol{x}_2) \varphi_k(\boldsymbol{x}_1) \varphi_l(\boldsymbol{x}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{21}$$

where φ's are spin orbitals spanning the active space.

2 Excitation energies of defects

In the following tables we list low-energy FCI solutions of the effective Hamiltonian for defects. VBM and CBM denote valence band maximum and conduction band minimum, respectively.

Table 1: Energies (eV), symmetries and characters of low-energy eigenstates obtained from FCI calculation of effective Hamiltonians for the NV center in diamond. Effective Hamiltonians are constructed within and beyond the random phase approximation (RPA). The ground state energy is set to zero. GS indicates ground state, GS-SF indicates spin-flip excitations within the ground state orbital configuration.

State	RPA			Beyond-RPA		
	Energy	Symmetry	Character	Energy	Symmetry	Character
0	0.000	$^3A_2$	GS	0.000	$^3A_2$	GS
1	0.476	^1E	GS-SF	0.561	^1E	GS-SF
2	1.376	$^1A_1$	GS-SF	1.759	$^1A_1$	GS-SF
3	1.921	^3E	$a_1 \rightarrow e$	2.001	^3E	$a_1 \rightarrow e$
4	2.996	^1E	$a_1 \rightarrow e$	3.461	^1E	$a_1 \rightarrow e$

Table 2: Energies (eV), symmetries and characters of low-energy eigenstates obtained from FCI calculation of effective Hamiltonians for the SiV in diamond. The ground state energy is set to zero. GS indicates ground state, GS-SF indicates spin-flip excitations within ground state orbital configurations.

State	RPA			Beyond-RPA		
	Energy	Symmetry	Character	Energy	Symmetry	Character
0	0.000	$^3A_{2g}$	GS	0.000	$^3A_{2g}$	GS
1	0.261	^1E_g	GS-SF	0.336	^1E_g	GS-SF
2	0.466	$^1A_{1g}$	GS-SF	0.583	$^1A_{1g}$	GS-SF
3	1.254	^3E_g	VBM $\rightarrow e_g$	1.347	^3E_g	VBM $\rightarrow e_g$
4	1.268	^1E_g	VBM $\rightarrow e_g$	1.363	^1E_g	VBM $\rightarrow e_g$
5	1.424	$^3A_{1g}$	$e'_g \rightarrow e_g$	1.508	$^3A_{1g}$	$e'_g \rightarrow e_g$
6	1.441	^3E_g	$e'_g \rightarrow e_g$	1.530	^3E_g	$e'_g \rightarrow e_g$
7	1.469	$^1A_{2g}$	$e'_g \rightarrow e_g$	1.563	$^1A_{2g}$	$e'_g \rightarrow e_g$
8	1.545	$^3A_{2g}$	$e'_g \rightarrow e_g$	1.583	$^3A_{2u}$	$e_u \rightarrow e_g$
9	1.587	$^3A_{2u}$	$e_u \rightarrow e_g$	1.594	^3E_u	$e_u \rightarrow e_g$
10	1.590	^3E_u	$e_u \rightarrow e_g$	1.623	$^1A_{1u}$	$e_u \rightarrow e_g$
11	1.608	$^1A_{1u}$	$e_u \rightarrow e_g$	1.636	$^3A_{2g}$	$e'_g \rightarrow e_g$
12	1.619	^1E_g	$e'_g \rightarrow e_g$	1.723	^1E_g	$e'_g \rightarrow e_g$
13	1.692	$^1A_{1g}$	$e'_g \rightarrow e_g$	1.792	$^3A_{1u}$	$e_u \rightarrow e_g$
14	1.741	$^3A_{1u}$	$e_u \rightarrow e_g$	1.812	$^1A_{1g}$	$e'_g \rightarrow e_g$
15	2.056	^1E_u	$e_u \rightarrow e_g$	2.171	^1E_u	$e_u \rightarrow e_g$
16	2.365	$^1A_{2u}$	$e_u \rightarrow e_g$	2.515	$^1A_{2u}$	$e_u \rightarrow e_g$

Table 3: Energies (eV), symmetries and characters of low-energy eigenstates obtained from FCI calculation of effective Hamiltonians for Cr in 4H-SiC. The ground state energy is set to zero. GS indicates ground state, GS-SF indicates spin-flip excitations within ground state orbital configuration. Excitations from e level to the CBM are positioned more than 3 eV above the ground state.

State	RPA			Beyond-RPA		
	Energy	Symmetry	Character	Energy	Symmetry	Character
0	0.000	$^3A_2$	GS	0.000	$^3A_2$	GS
1	0.860	^1E	GS-SF	1.090	^1E	GS-SF
2	1.365	^3E	$e \rightarrow t'$	1.304	^3E	$e \rightarrow t'$
3	1.480	$^3A_1$	$e \rightarrow t'$	1.406	$^3A_1$	$e \rightarrow t'$
4	1.560	$^1A_1$	GS-SF	1.704	^3E	$e \rightarrow t'$
5	1.597	^3E	$e \rightarrow t'$	1.755	$^3A_2$	$e \rightarrow t'$
6	1.635	$^3A_2$	$e \rightarrow t'$	1.937	$^1A_1$	GS-SF
7	1.770	^1E	$e \rightarrow t'$	1.948	^1E	$e \rightarrow t'$

3 Convergence of the active space size

In the main text we report results obtained with active spaces sufficiently large to converge the excitation energies; they include 21/38/23 spatial orbitals (42/76/46 spin orbitals) for NV/SiV/Cr defects, respectively. As an example, in Fig. 1 we show the convergence of FCI eigenvalues of the NV center as a function of the size of the active space. The minimum model $\{a_1, e\}$ already yields excitation energies within 0.2 eV of the converged results, and is used for quantum simulations reported in the main text. Inclusion of a_1' level and other valence band states near the VBM yields results that converge rapidly. Including empty states does not affect the computed excitation energies.

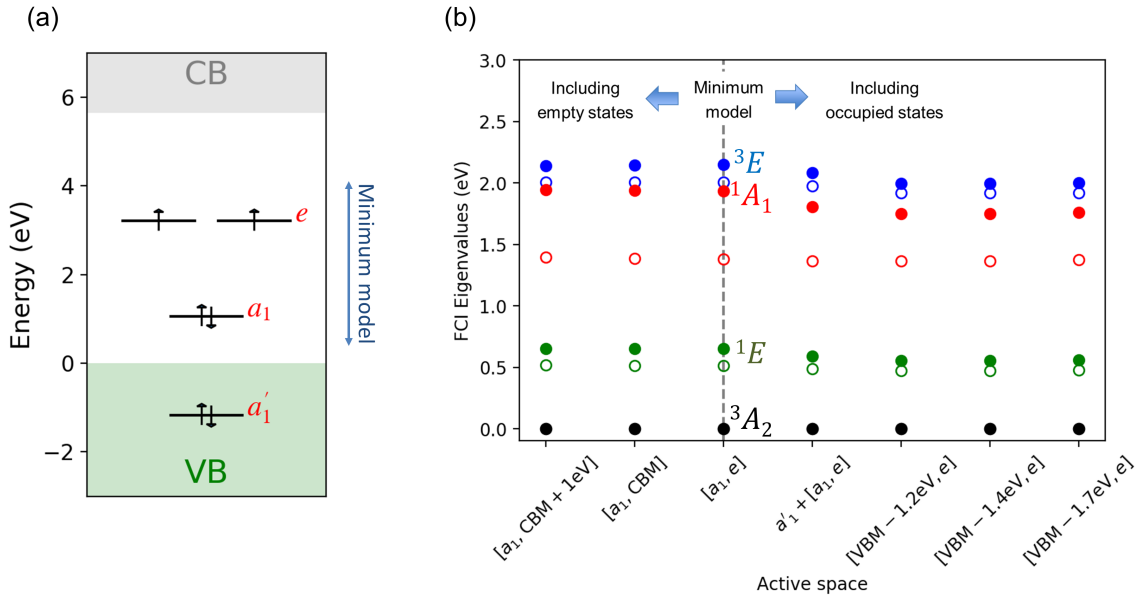

Figure 1: (a) Single-particle level diagrams for the NV center in diamond. The minimum model for the NV center includes the a_1 and e levels in the band gap. (b) Convergence of FCI eigenvalues as functions of the size of active space (represented by intervals between the lowest and highest single-particle levels). Empty and full circles represent RPA and beyond-RPA results, respectively.

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