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Quantum simulations of materials on near-term quantum computers

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Quantum computers hold promise to enable efficient simulations of the properties of molecules and materials; however, at present they only permit ab initio calculations of a few atoms, due to a limited number of qubits. In order to harness the power of near-term quantum computers for simulations of larger systems, it is desirable to develop hybrid quantum-classical methods where the quantum computation is restricted to a small portion of the system. This is of particular relevance for molecules and solids where an active region requires a higher level of theoretical accuracy than its environment. Here, we present a quantum embedding theory for the calculation of strongly-correlated electronic states of active regions, with the rest of the system described within density functional theory. We demonstrate the accuracy and effectiveness of the approach by investigating several defect quantum bits in semiconductors that are of great interest for quantum information technologies. We perform calculations on quantum computers and show that they yield results in agreement with those obtained with exact diagonalization on classical architectures, paving the way to simulations of realistic materials on near-term quantum computers.

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INTRODUCTION

In the last three decades, atomistic simulations based on the solution of the basic equation of quantum mechanics have played an increasingly important role in predicting the properties of functional materials, encompassing catalysts and energy storage systems for energy applications, and materials for quantum information science. Especially in the case of complex, heterogeneous materials, the great majority of first-principles simulations are conducted using density functional theory (DFT), which is in principle exact but in practice requires approximations to enable calculations. Within its various approximations, DFT has been extremely successful in predicting numerous properties of solids, liquids, and molecules, and in providing key interpretations to a variety of experimental results; however it is often inadequate to describe so-called strongly-correlated electronic states^{1,2}. We will use here the intuitive notion of strong correlation as pertaining to electronic states that cannot be described by static mean-field theories. Several theoretical and computational methods have been developed over the years to treat systems exhibiting strongly-correlated electronic states, including dynamical mean-field theory^{3,4} and quantum Monte-Carlo^{5,6}; in addition, ab initio quantum chemistry methods, traditionally developed for molecules, have been recently applied to solid state problems as well⁷. Unfortunately, these approaches are computationally demanding and it is still challenging to apply them to complex materials containing defects and interfaces, even using high-performance computing architectures.

Quantum computers hold promise to enable efficient quantum mechanical simulations of weakly and strongly-correlated molecules and materials alike^{8–17}; in particular when using quantum computers, one is able to simulate systems of interacting electrons exponentially faster than using classical computers. Thanks to

decades of successful experimental efforts, we are now entering the noisy intermediate-scale quantum (NISQ) era¹⁸, with quantum computers expected to have on the order of 100 quantum bits (qubits); unfortunately this limited number of qubits still prevents straightforward quantum simulations of realistic molecules and materials, whose description requires hundreds of atoms and thousands to millions of degrees of freedom to represent the electronic wavefunctions. An important requirement to tackle complex chemistry and material science problems using NISQ computers is the reduction of the number of electrons treated explicitly at the highest level of accuracy^{19,20}. For instance, building on the idea underpinning dynamical mean field theory (DMFT)^{3,4}, one may simplify complex molecular and material science problems by defining active regions (or building blocks) with strongly-correlated electronic states, embedded in an environment that may be described within mean-field theory^{21–23}.

In this work, we present a quantum embedding theory built on DFT, which is scalable to large systems and which includes the effect of exchange-correlation interactions of the environment on active regions, thus going beyond commonly adopted approximations. In order to demonstrate the effectiveness and accuracy of the theory, we compute ground and excited state properties of several spin-defects in solids including the negatively charged nitrogen-vacancy (NV) center^{24–30}, the neutral silicon-vacancy (SiV) center^{31–36} in diamond, and the Cr impurity (4+) in 4H-SiC^{37–39}. These spin-defects are promising platforms for solid-state quantum information technologies, and they exhibit strongly-correlated electronic states that are critical for the initialization and read-out of their spin states^{40–45}. Our quantum embedding theory yields results in good agreement with existing measurements. In addition, we present theoretical predictions for the position and ordering of the singlet states of SiV and of Cr, and we

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provide an interpretation of experiments that have so far remained unexplained.

Importantly, we report calculations of spin-defects using a quantum computer^{46,47}. Based on the effective Hamiltonian derived from the quantum embedding theory, we investigated the strongly-correlated electronic states of the NV center in diamond using quantum phase estimation algorithm (PEA)^{8,48} and variational quantum eigensolvers (VQE)^{49–51}, and we show that quantum simulations yield results in agreement with those obtained with classical full configuration interaction (FCI) calculations. Our findings pave the way to the use of near term quantum computers to investigate the properties of realistic heterogeneous materials with first-principles theories.

RESULTS

General strategy

We summarize our strategy in Fig. 1. Starting from an atomistic structural model of materials (e.g., obtained from DFT calculations or molecular dynamics simulations), we identify active regions with strongly-correlated electrons, which we describe with an effective Hamiltonian that includes the effect of the environment on the active region. This effective Hamiltonian is constructed using the quantum embedding theory described below, and its eigenvalues can be obtained by either classical algorithms such as exact diagonalization (FCI) or quantum algorithms.

Embedding theory

A number of interesting quantum embedding theories have been proposed over the past decades⁵². For instance, density functional embedding theory has been developed to improve the accuracy and scalability of DFT calculations^{53–57}. Density matrix embedding theory (DMET)^{58–60} and various Green's function based approaches^{61,62}, e.g., DMFT, have been developed to describe systems with strongly-correlated electronic states. At present, ab initio calculations of materials using DMET and DMFT have been limited to relatively small unit cells (a few tens of atoms) of pristine crystals, due to their high computational cost^{63,64}. In this work, we present a quantum embedding theory that is applicable to strongly-correlated electronic states in realistic heterogeneous materials and we apply it to systems with hundreds of atoms. The theory, inspired by the constrained random phase approximation (cRPA) approach^{65–67}, does not require the explicit evaluation of virtual electronic states^{68,69}, thus making the method scalable to materials containing thousands of electrons. Furthermore, cRPA approaches contain a specific approximation (RPA) to the screened Coulomb interaction, which neglects exchange-correlation effects and may lead to inaccuracies in the description of dielectric screening. Our embedding theory goes beyond the

RPA by explicitly including exchange-correlation effects, which are evaluated with a recently developed finite-field algorithm^{70,71}.

The embedding theory developed here aims at constructing an effective Hamiltonian operating on an active space (A), defined as a subspace of the single-particle Hilbert space:

$$H^{\text{eff}} = \sum_{ij}^A t_{ij}^{\text{eff}} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl}^A V_{ijkl}^{\text{eff}} a_i^\dagger a_j^\dagger a_l a_k. \quad (1)$$

Here, t^{eff} and V^{eff} are one-body and two-body interaction terms that take into account the effect of all the electrons that are part of the environment (E) in a mean-field fashion, at the DFT level. An active space can be defined, for example, by solving the Kohn–Sham equations of the full system and selecting a subset of eigenstates among which electronic excitations of interest take place (e.g., defect states within the gap of a semiconductor or insulator). To derive an expression for V^{eff} that properly accounts for all effects of the environment including exchange and correlation interactions, we define the environment density response function (reducible polarizability) $\chi^E = \chi_0^E + \chi_0^E f \chi^E$, where $\chi_0^E = \chi_0 - \chi_0^A$ is the difference between the polarizability of the Kohn–Sham system χ_0 and its projection onto the active space χ_0^A (see Supplementary Information (SI)). χ^E thus represents the density response outside the active space. The term $f = V + f_{\text{xc}}$ is often called the Hartree-exchange-correlation kernel, where V is the Coulomb interaction and the exchange-correlation kernel f_{xc} is defined as the derivative of the exchange-correlation potential with respect to the electron density. We define the effective interactions between electrons in A as

$$V^{\text{eff}} = V + f \chi^E f, \quad (2)$$

given by the sum of the bare Coulomb potential and a polarization term arising from the density response in the environment E. When the RPA is adopted, the exchange-correlation kernel f_{xc} is neglected in Eq. (2) and the expression derived here reduces to that used within cRPA. We represent χ^E and f on a compact basis obtained from a low-rank decomposition of the dielectric matrix^{68,69} that allows us to avoid the evaluation and summation over virtual electronic states. Once V^{eff} is defined, the one-body term t^{eff} can be computed by subtracting from the Kohn–Sham Hamiltonian a term that accounts for Hartree and exchange-correlation effects in the active space (see SI).

Embedding theory applied to spin-defects

The embedding theory presented above is general and can be applied to a variety of systems for which active regions, or building blocks, with strongly-correlated electronic states may be identified: for example active sites in inorganic catalysts or organic molecules or defects in solids and liquids (e.g., solvated ions in water). Here we apply the theory to spin-defects including NV and SiV in diamond and Cr in 4H-SiC. Most of these defects' excited

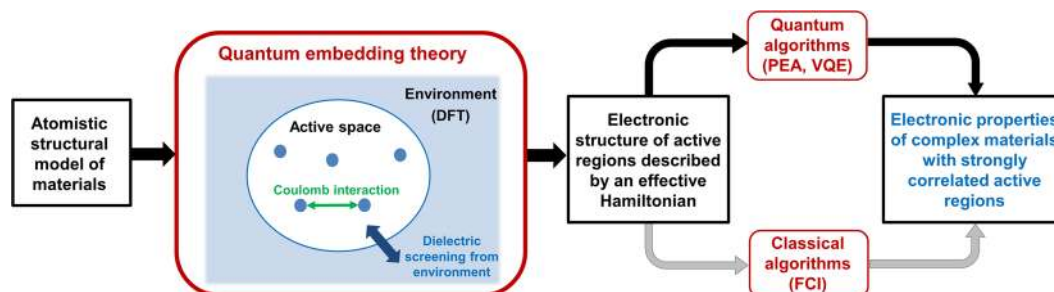


Fig. 1 General strategy for quantum simulations of materials using quantum embedding. The full system is separated into an active space and its environment, with the electronic states in the active space described by an effective Hamiltonian solved with either classical (e.g., full configuration interaction, FCI) or quantum algorithms (e.g., phase estimation algorithm (PEA), variational quantum eigensolver (VQE)). The effective interaction between electrons in the active space includes the bare Coulomb interaction and a polarization term arising from the dielectric screening of the environment (see text), which is evaluated including exchange-correlation interactions.

states are strongly-correlated (they cannot be represented by a single Slater determinant of single-particle orbitals), as shown e.g., for the NV center in diamond by Bockstedte et al.⁷² using cRPA calculations. We demonstrate that our embedding theory can successfully describe the many-body electronic structure of different types of defects including transition metal atoms; our results not only confirm existing experimental observations but also provide a detailed description of the electronic structure of defects not presented before, which sheds light into their optical cycles.

We first performed spin-restricted DFT calculations using hybrid functionals⁷³ to obtain a mean-field description of the defects and of the whole host solid. The spin restriction ensures that both spin channels are treated on an equal footing and that there is no spin-contamination when building effective Hamiltonians. Based on our DFT results, we then selected active spaces that include single-particle defect wavefunctions and relevant resonant and band edge states. We verified that the size of the chosen active spaces yields converged excitation energies (see SI). We then constructed effective Hamiltonians (Eqs. (1)–(2)) by taking into account exchange-correlation effects, and we obtained many-body ground and excited states using classical (FCI) and, for selected cases, quantum algorithms (PEA, VQE). All calculations were performed at the spin triplet ground state geometries obtained by spin-unrestricted DFT calculations, thus obtaining vertical excitation energies (equal to the sums of zero phonon line (ZPL) and Stokes energies). It is straightforward to extend the current approach to compute potential energy surfaces at additional geometries¹, so as to include relaxations and Jahn–Teller effects^{36,72}. In Fig. 2 we present atomistic structures, single-particle defect levels, and the many-body electronic structure of three spin-defects. Several relevant vertical excitation energies are reported in Table 1, and additional ones are given in the SI. In the following discussion, lower-case symbols represent single-particle states obtained from DFT and upper-case symbols represent many-body states.

For the NV in diamond, we constructed effective Hamiltonians (Eq. (1)) by using an active space that includes a_1 and e single-particle defect levels in the band gap and states near the valence band maximum (VBM). Our FCI calculations correctly yield the symmetry and ordering of the low-lying 3A_2 , 3E , 1E and 1A_1 states. The vertical excitation energies reported in Table 1 show that including exchange-correlation effects yields results in better agreement with experiments than those obtained within the RPA. The results obtained within RPA (0.476/1.376/1.921 eV for ${}^1E/{}^1A_1/{}^3E$ states) are in good agreement with cRPA results reported in⁷² (0.47/1.41/2.02 eV).

In the case of the SiV in diamond, we built effective Hamiltonians using an active space with the e_u and e_g defect levels and states near the VBM, including resonant e'_u and e'_g states. Effective Hamiltonians including or neglecting exchange-correlation effects yield similar results, with the excitation energies obtained beyond RPA being slightly higher. We predicted the first optically-allowed excited state to be a 3E_u state with vertical excitation energy of 1.59 eV, in good agreement with the sum of 1.31 eV ZPL measured experimentally³¹ and 0.258 eV Stokes shift estimated using an electron-phonon model³⁶. Our calculations predicted a ${}^3A_{2u}$ state 11 meV below the 3E_u state, in qualitative agreement with a recent experimental observation by Green

et al.³⁵, which proposed a ${}^3A_{2u}$ - 3E_u manifold with 7 meV separation in energy. The small difference in energy splitting between our results and experiment is likely due to geometry relaxation effects are not yet taken into account in our study. In addition to states of u symmetry generated by $e_u \rightarrow e_g$ excitations, we observed a number of optically dark states of g symmetry (gray levels in Fig. 2b) originating from the excitation from the e'_g level and the VBM states to the e_g level.

Despite significant efforts^{33–36}, several important questions on the singlet states of SiV remain open. These states are crucial for a complete understanding of the optical cycle of the SiV center. Our predicted ordering of singlet states of SiV is shown in Fig. 2b. We find the vertical excitation energies of the ${}^1A_{1u}$ state to be slightly higher than that of the ${}^3A_{2u}$ - 3E_u triplet manifold, suggesting that the intersystem crossing (ISC) from ${}^3A_{2u}$ or 3E_u to singlet states may be energetically unfavorable (first-order ISC to lower 1E_g and ${}^1A_{1g}$ states are forbidden). We note that the 1E_u and ${}^1A_{2u}$ states are much higher in energy than ${}^1A_{1u}$ and are not expected to play a significant role in the optical cycle. In addition the first-order ISC process from the lowest energy singlet state 1E_g to the ${}^3A_{2g}$ ground state is forbidden by symmetry. Overall our results indicate that the ${}^3A_{2g}$ state is populated through higher-order processes and therefore the spin-selectivity of the full optical cycle is expected to be low. While more detailed studies including spin-orbit coupling are required for definitive conclusions, our predictions shed light on the strongly-correlated singlet states of SiV and provide a possible explanation for the experimental difficulties in measuring optically-detected magnetic resonance of SiV.

We now turn to Cr in 4H-SiC, where we considered the hexagonal configuration. We constructed effective Hamiltonians with the half-filling e level in the band gap and states near the conduction band minimum including resonance states. Upon solving the effective Hamiltonian, we predict the lowest excited state to be a 1E state arising from $e \rightarrow e$ spin-flip transition, with excitation energy of 1.09 (0.86) eV based on embedding calculations beyond (within) the RPA. Results including exchange-correlation effects are in better agreement with the measured ZPL of 1.19 eV³⁷, where the Stokes energy is expected to be small given the large Debye-Waller factor³⁹. There is currently no experimental report for the triplet excitation energies of Cr in 4H-SiC, but our results are in good agreement with existing experimental measurements for Cr in GaN, a host material with a crystal field strength similar to that of 4H-SiC³⁸. We predict the existence of a ${}^3E + {}^3A_1$ manifold at ≈ 1.4 eV and a ${}^3E' + {}^3A_2'$ manifold at ≈ 1.7 eV above the ground state (Fig. 2c), resembling the 3T_2 manifold (1.2 eV) and 3T_1 manifold (1.6 eV) for Cr in GaN observed experimentally⁷⁴. We note that in many cases it is challenging to study materials containing transition metal elements with DFT⁷⁵. The agreement between FCI results and experimental measurements clearly demonstrates that the embedding theory developed here can effectively describe the strongly-correlated part of the system, while yielding at the same time a quantitatively correct description of the environment.

Quantum simulations of spin-defects

The results presented in the previous section were obtained using classical algorithms. We now turn to the use of quantum algorithms. To perform quantum simulations with PEA and VQE, we constructed a minimum model of an NV center including only a_1 and e orbitals in the band gap. This model (four electrons in six spin orbitals) yields excitation energies within 0.2 eV of the converged results using a larger active space. In Fig. 3 we show the results of quantum simulations.

We first performed PEA simulations with a quantum simulator (without noise)⁴⁶ to compute the energy of 3A_2 , 3E , 1E , and 1A_1 states. We used molecular orbital approximations of these states

¹For example, one may follow the strategy of ref. ⁷² and compute excited states of defects along given normal modes, which are usually obtained from delta-SCF calculations. This type of treatment, albeit approximate, provides valuable insights into the vibrational properties of defects in excited states.

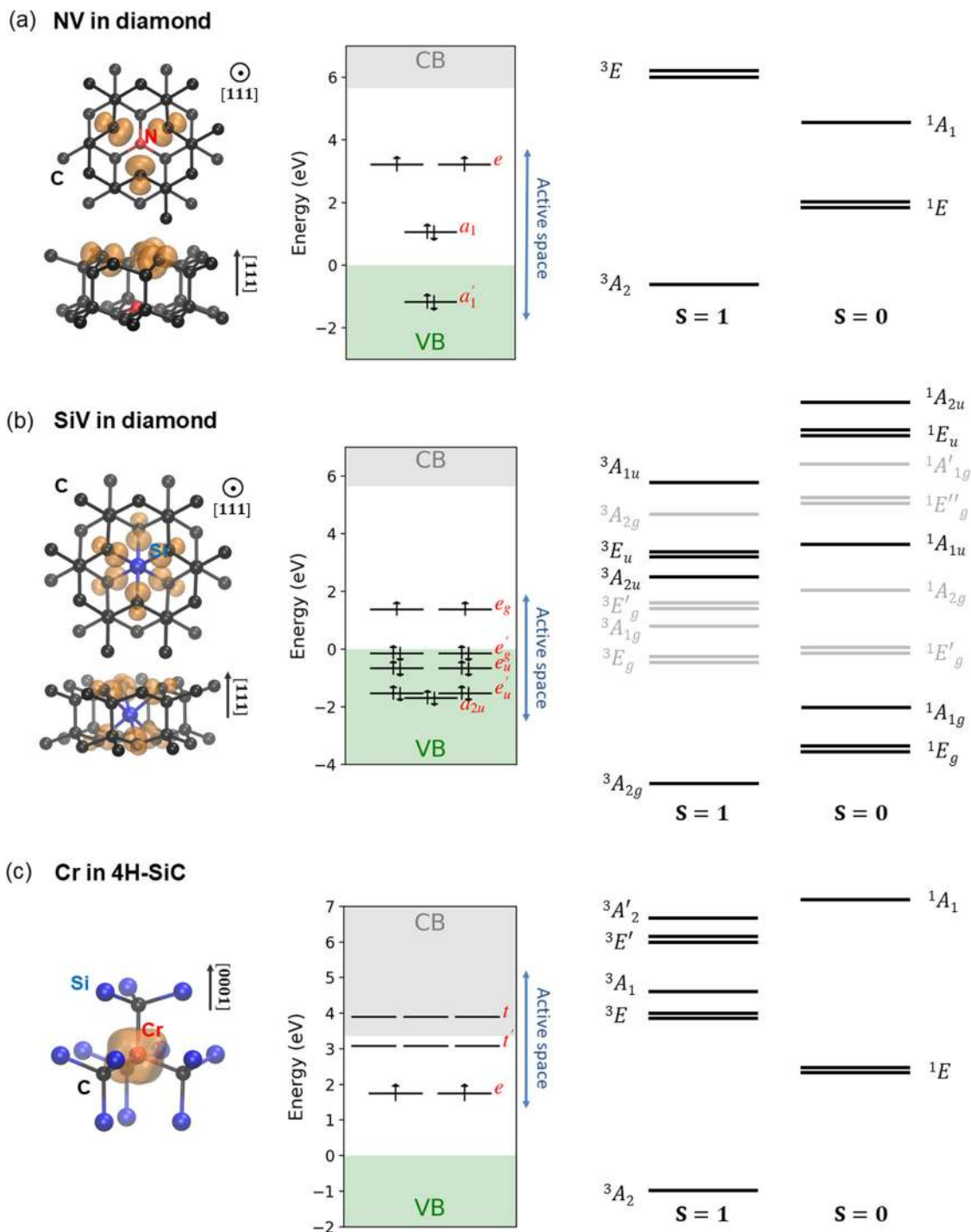


Fig. 2 Electronic structure of spin-defects. (a), (b), and (c) present results for the negatively-charged nitrogen vacancy (NV) in diamond, the neutral silicon vacancy (SiV) in diamond, and the Cr impurity (4+) in 4H-SiC, respectively. Left panels show spin densities obtained from spin unrestricted DFT calculations. Middle panels show the position of single-particle defect levels computed by spin restricted DFT calculations. States included in active spaces (see text) are indicated by blue vertical lines. Right panels show the symmetry and ordering of the low-lying many-body electronic states obtained by exact diagonalization (FCI calculations) of effective Hamiltonians constructed with exchange-correlation interactions included.

derived from group theory²⁶ as initial states for PEA, which are single Slater determinant for 3A_2 ($M_S = 1$) and 3E ($M_S = 1$) states, and superpositions of two Slater determinants for 1E and 1A_1 states. As shown in Fig. 3a, PEA results converge to classical FCI results with an increasing number of ancilla qubits.

We then performed VQE simulations with a quantum simulator and with the IBM Q 5 Yorktown quantum computer⁴⁷. We

estimated the energy of the 3A_2 ground state manifold by performing VQE calculations for both the single-Slater-determinant $M_S = 1$ component and the strongly-correlated $M_S = 0$ component. Within a molecular orbital notation, $M_S = 1$ and $M_S = 0$ ground states can be represented as $|a\bar{a}e_xe_y\rangle$ and $\frac{1}{\sqrt{2}}(|a\bar{a}e_x\bar{e}_y\rangle + |a\bar{a}\bar{e}_xe_y\rangle)$, respectively, where a , e_x , e_y (spin-up) and

Table 1. Vertical excitation energies (eV) of the negatively charged nitrogen vacancy (NV) and neutral silicon vacancy (SiV) in diamond and Cr (4+) in 4H-SiC, obtained using the random phase approximation (RPA: third column) and including exchange-correlation interactions (beyond RPA: fourth column). Experimental measurements of zero-phonon-line (ZPL) energies are shown in brackets in the fifth column. Reference vertical excitation energies are computed from experimental ZPL when Stokes energies are available.

System	Excitation	RPA	Beyond-RPA	Expt.
NV	${}^3A_2 \leftrightarrow {}^3E$	1.921	2.001	2.180 ^a (1.945 ^a)
	${}^3A_2 \leftrightarrow {}^1A_1$	1.376	1.759	
	${}^3A_2 \leftrightarrow {}^1E$	0.476	0.561	
	${}^1E \leftrightarrow {}^1A_1$	0.900	1.198	(1.190 ^b)
	${}^1A_1 \leftrightarrow {}^3E$	0.545	0.243	(0.344–0.430 ^c)
SiV	${}^3A_{2g} \leftrightarrow {}^3E_u$	1.590	1.594	1.568 ^d (1.31 ^e)
	${}^3A_{2g} \leftrightarrow {}^3A_{1u}$	1.741	1.792	
	${}^3A_{2g} \leftrightarrow {}^1E_g$	0.261	0.336	
	${}^3A_{2g} \leftrightarrow {}^1A_{1g}$	0.466	0.583	
	${}^3A_{2g} \leftrightarrow {}^1A_{1u}$	1.608	1.623	
	${}^3A_{2g} \leftrightarrow {}^1E_u$	2.056	2.171	
	${}^3A_{2g} \leftrightarrow {}^1A_{2u}$	2.365	2.515	
	${}^3A_{2u} \leftrightarrow {}^3E_u$	0.003	0.011	(0.007 ^e)
Cr	${}^3A_2 \leftrightarrow {}^3E$	1.365	1.304	
	${}^3A_2 \leftrightarrow {}^3A_1$	1.480	1.406	
	${}^3A_2 \leftrightarrow {}^3E'$	1.597	1.704	
	${}^3A_2 \leftrightarrow {}^3A'_2$	1.635	1.755	
	${}^3A_2 \leftrightarrow {}^1E$	0.860	1.090	(1.190 ^f)
	${}^3A_2 \leftrightarrow {}^1A_1$	1.560	1.937	

^aRef. 24.
^bRef. 25.
^cEstimated by Ref. 30 with a model for intersystem crossing.
^dComputed with Stokes energy from Ref. 36.
^eRef. 35.
^fRef. 37.

\bar{a} , \bar{e}_x , \bar{e}_y (spin-down) denote a_1 and e orbitals. To obtain the $M_S = 0$ ground state, we used a closed-shell Hartree–Fock state $|a\bar{a}e_x\bar{e}_x\rangle$ as reference; the $M_S = 1$ ground state is itself an open-shell Hartree–Fock state, so we started with a higher energy reference state $|ae_x\bar{e}_xe_y\rangle$ in the 3E manifold. We used unitary coupled-cluster single and double (UCCSD) ansatzes⁴⁹ to represent the trial wavefunctions. Fig. 3b and c shows the estimated ground state energy as a function of the number of VQE iterations, where VQE calculations performed with the quantum simulator correctly converges to the ground state energy in both the $M_S = 1$ and $M_S = 0$ case. Despite the presence of noise, whose characterization and study will be critical to improve the use of quantum algorithms⁷⁶, the results obtained with the quantum computer converge to the ground state energy within a 0.2 eV error. Calculations of excited states with quantum algorithms will be the focus of future works.

DISCUSSION

With the goal of providing a strategy to solve complex materials problems on NISQ computers, we proposed a first-principles quantum embedding theory where appropriate active regions of a material and their environment are described with different levels of accuracy, and the whole system is treated quantum mechanically. In particular, we used hybrid DFT for the environment, and we built a many-body Hamiltonian for the active space with

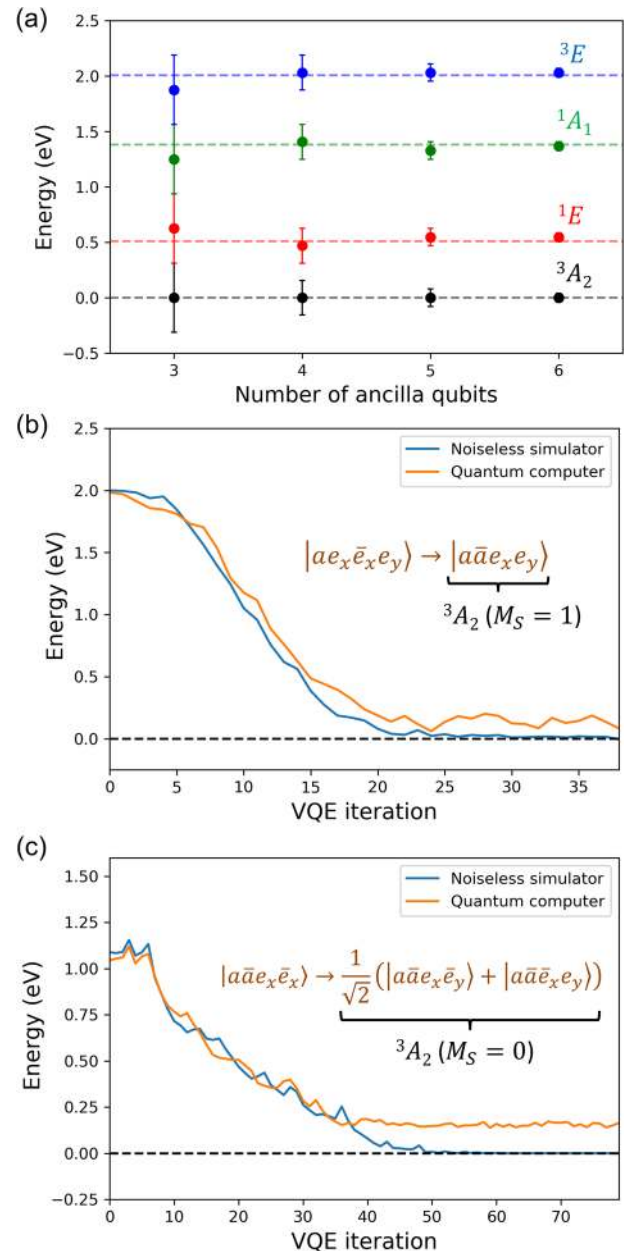


Fig. 3 Quantum simulations of a minimum model of the NV center in diamond using the phase estimation algorithm (PEA) and a variational quantum eigensolver (VQE). The energy of the 3A_2 ground state manifold is set to zero for convenience. **a** PEA estimation of ground and excited states of the NV center. Error bars represent the uncertainties due to the finite number of ancilla qubits used in the simulations; dashed lines show classical FCI results. **b** VQE estimation of ground state energy, starting from $|ae_x\bar{e}_xe_y\rangle$ state ($M_S = 1$, see text). **c** VQE estimation of ground state energy, starting from $|a\bar{a}e_x\bar{e}_x\rangle$ state ($M_S = 0$); strongly-correlated $\frac{1}{\sqrt{2}}(|a\bar{a}e_x\bar{e}_y\rangle + |a\bar{a}\bar{e}_xe_y\rangle)$ state ($M_S = 0$ state in the 3A_2 manifold) is obtained with VQE.

effective electron–electron interactions that include dielectric screening and exchange–correlation effects from the environment. Our method overcomes the commonly used random phase approximation, which neglects exchange–correlation effects; importantly it is applicable to heterogeneous materials and scalable to large systems, due to the algorithms used here to compute response functions^{70,71}. We emphasize that the

embedding theory presented here provides a flexible framework where multiple effects of the environment may be easily incorporated. For instance, dynamical screening effects can be included by considering a frequency-dependent screened Coulomb interaction, evaluated using the same procedure as the one outlined here for static screening; electron-phonon coupling effects can be incorporated by including phonon contributions in the screened Coulomb interactions. Furthermore, for systems where the electronic structure of the active region is expected to influence that of the host material, a self-consistent cycle in the calculation of the screened Coulomb interaction of the environment can be easily added to the approach.

We presented results for spin-defects in semiconductors obtained with both classical and quantum algorithms, and we showed excellent agreement between the two sets of techniques. Importantly, for selected cases we showed results obtained using a quantum simulator and a quantum computer, which agree within a relatively small error, in spite of the presence of noise in the quantum hardware. We made several predictions for excited states of SiV in diamond and Cr in SiC, which provide important insights into their full optical cycle. We also demonstrated that a treatment of the dielectric screening beyond the random phase approximation leads to an accurate prediction of excitation energies.

The method proposed in our work enables calculations of realistic, heterogeneous materials using the resources of NISQ computers. We demonstrated quantum simulations of strongly-correlated electronic states in considerably larger systems (with hundreds of atoms) than previous studies combining quantum simulation and quantum embedding^{19–23}. We have studied solids with defects, not just pristine materials, which are of great interest for quantum technologies. The strategy adopted here is general and may be applied to a variety of problems, including the simulation of active regions in molecules and materials for the understanding and discovery of catalysts and new drugs, and of aqueous solutions containing complex dissolved species. We finally note that our approach is not restricted to strongly-correlated active regions and will be useful also in the case of weakly correlated systems, where different regions of a material may be treated with varying levels of accuracy. Hence we expect the strategy presented here to be widely applicable to carry out quantum simulations of materials on near-term quantum computers.

METHODS

Density functional theory

All ground state DFT calculations are performed with the Quantum Espresso code⁷⁷ using the plane-wave pseudopotential formalism. Electron-ion interactions are modeled with norm-conserving pseudopotentials from the SG15 library⁷⁸. A kinetic energy cutoff of 50 Ry is used. All geometries are relaxed with spin-unrestricted DFT calculations using the Perdew-Burke-Ernzerhof (PBE) functional⁷⁹ until forces acting on atoms are smaller than 0.013 eV / Å. NV and SiV in diamond are modeled with 216-atom supercells; Cr in 4H-SiC is modeled with a 128-atom supercell. The Brillouin zone is sampled with the Γ point.

Construction of effective Hamiltonians

Construction of effective Hamiltonians is performed with the WEST code⁶⁹, starting from wavefunctions of spin-restricted DFT calculations. For this step, we remark that the use of hybrid functional is important for an accurate mean-field description of defect levels, even though the geometry of defects are well represented at the PBE level. We used a dielectric dependent hybrid (DDH) functional⁷³ which self-consistently determines the fraction of exact exchange based on the dielectric constant of the host material. In particular, 17.8% and 15.2% of exact exchange were used for the calculations of defects in diamond and 4H-SiC, respectively. The DDH functional was shown to yield accurate band gaps of diamond and silicon carbide, as well as optical properties of defects^{41,42,80–82}. After

hybrid functional solutions of the Kohn–Sham equations are obtained, iterative diagonalizations of χ_0 are performed, and density response functions and f_{xc} of the system are represented on a basis consisting of the first 512 eigenpotentials of χ_0 . Finite field calculations of f_{xc} are performed by coupling the WEST code with the Qbox⁸³ code. FCI calculations⁸⁴ on the effective Hamiltonian are carried out using the PySCF⁷ code.

Quantum simulations

In order to carry out quantum simulations, a minimum model of the NV center is constructed by applying the embedding theory with a_1 and e orbitals beyond the RPA.

In PEA simulations, the Jordan–Wigner transformation⁸⁵ is used to map the fermionic effective Hamiltonian to a qubit Hamiltonian, and Pauli operators with prefactors smaller than 10^{-6} a.u. are neglected to reduce the circuit depth, which results in less than 10^{-4} a.u. (0.003 eV) change in eigenvalues. In order to achieve optimal precision, the Hamiltonian is scaled such that 0 and 2.5 eV are mapped to phases $\phi = 0$ and $\phi = 1$ of the ancilla qubits, respectively. We used the first-order Trotter formula to split time evolution operators into 4 time slices.

In VQE simulations, the parity transformation⁹ is adopted. For the simulation of the $M_S = 1$ state, the resulting qubit Hamiltonian acts on four qubits and there are two variational parameters in the UCCSD ansatz. For the simulation of the $M_S = 0$ state, we fixed the occupation of the a orbital and the resulting qubit Hamiltonian acts on 2 qubits. We replicated the exponential excitation operator twice, with parameters in both replicas variationally optimized. Such a choice results in six variational parameters, providing a sufficient number of degrees of freedom for an accurate representation of the strongly-correlated $M_S = 0$ state. Parameters in the ansatz are optimized with the COBYLA algorithm⁸⁶.

Quantum simulations are performed with the QASM simulator and the IBM Q 5 Yorktown quantum computer using the IBM Qiskit package⁴⁶. Each quantum circuit is executed 8192 times to obtain statistically reliable sampling of the measurement results.

DATA AVAILABILITY

Data that support the findings of this study are available through the Qresp⁸⁷ curator at <https://doi.org/10.6084/m9.figshare.12501407>.

CODE AVAILABILITY

The quantum embedding theory is implemented in the open source code WEST (west-code.org/).

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AUTHOR CONTRIBUTIONS

H.M., M.G., and G.G. designed the research. H.M. implemented the quantum embedding theory and performed simulations with classical and quantum algorithms, with supervision by M.G. and G.G. All authors wrote the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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