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The energetics of point defects in oxide materials plays a major role in determining their high-temperature properties, but experimental measurements are difficult, and calculations based on density functional theory (DFT) are not necessarily reliable. We report quantum Monte Carlo (QMC) calculations of the formation energy E_S of Schottky defects in MgO, which demonstrate the feasibility of using this approach to overcome the deficiencies of DFT. In order to investigate system-size errors, we also report DFT calculations of E_S on repeating cells of up to ~ 1000 atoms, which indicate that QMC calculations on systems of only 54 atoms should yield high precision. The DFT calculations also provide the relaxed structures used in the variational and diffusion Monte Carlo calculations. For MgO, we find E_S to be in close agreement with results from DFT and from model interaction potentials, and consistent with the scattered experimental values. The prospects for applying the same approach to transition metal oxides such as FeO are indicated.

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The quantum Monte Carlo (QMC) technique [1] is important in condensed matter science, because it is generally much more accurate than density functional theory (DFT) and allows one to make accurate predictions for problems where DFT fails [2–6]. It is usually competitive in accuracy with high-level quantum chemistry methods, but it has the advantage of being practicable for large systems containing hundreds of atoms. Recently, efforts have been made to apply QMC to oxide systems, including transition metal oxides [7,8], for which DFT gives poor predictions for magnetic properties, phonon frequencies and other properties [9]. We have recently reported [10] a QMC study of bulk MgO for which we find excellent agreement with experiments for the bulk lattice parameter and bulk modulus, provided appropriate corrections are made. We report here what we believe to be the first QMC calculation of an oxide lattice defect energy, namely the Schottky formation energy E_S in MgO. Defect energies in oxide materials are technologically important for applications ranging from high-temperature superconductors to radioactive waste disposal, but are also very difficult to measure experimentally. We shall show that our results for E_S in MgO are consistent with available experimental data, as well as supporting earlier DFT predictions [11].

The Schottky energy E_S is the energy required to form a cation and anion vacancy pair, and governs the thermal equilibrium concentration of vacancies [12]. The calculation of E_S in ionic materials has a very long history, going back to the very early work of Mott and Littleton [13–15]. DFT calculations on defect formation and migration energies in oxides first became possible in the early 1990's, and are now routinely performed. However, particularly in transition metal oxides, the reliability of DFT calculations is questionable.

QMC calculations are usually performed in two stages [1]. In the first, known as variational Monte Carlo (VMC), a trial many-body wavefunction is constructed as a product of a Slater determinant of single-electron orbitals and the so-called Jastrow factor which explicitly accounts for electronic correlation. Since VMC by itself is not usually accurate enough, the second stage is to use the many electron wavefunction produced by VMC in diffusion Monte Carlo (DMC), which improves the ground state estimate by performing an evolution in imaginary time. This would yield the exact ground-state energy but for the fact that the trial wavefunction fixes the nodes of the many-body wavefunction. Because of this, the DMC energy is an upper bound to the true ground-state energy, but for systems with a large band gap the difference is expected to be very small.

QMC calculations of defect energies in any material are challenging, and their feasibility is not obvious, for several reasons. First, it is not yet routinely possible to perform structural relaxation with QMC, and relaxation around defects produces a very large energy lowering in ionic materials [13–15]. Second, defect energies must be obtained as a difference of two large energies, both of which suffer the statistical errors inevitable with Monte Carlo methods. Third, there is a system size error associated with the limited size of the periodically repeated cell used in condensed-matter QMC calculations, and the difficulty of going to very large cell sizes makes it difficult to assess the error. To overcome these problems, we employ DFT calculations in tandem with QMC. In particular, the relaxed ionic positions used for QMC calculations on the defective crystals are taken from DFT calculations.

The overall strategy for our calculations is as follows. The Schottky energy E_S is defined to be the energy change when a Mg^{2+} ion and an O^{2-} ion are removed

from the MgO perfect crystal, the resulting defective crystal is allowed to relax, and the removed ions are replaced to form new perfect crystal. The two vacancies formed in this process are supposed to be very far apart, so that there is no interaction between them. In calculating E_S , either by DFT or by QMC, it is preferable to perform calculations in which no more than a single vacancy, either a Mg^{2+} vacancy or an O^{2-} vacancy, is present. We avoid doing calculations with both vacancies present in the same system, because with the cell sizes that can be achieved in practice, such calculations would suffer from a large unwanted interaction between the vacancies. Denoting by $E_N(\nu^+, \nu^-)$ the relaxed total energy of a crystal containing N cation lattice sites and N anion lattice sites, and with ν^+ cation vacancies and ν^- anion vacancies, we therefore express the Schottky energy as $E_S = E_N(1, 0) + E_N(0, 1) - [2(N - 1)/N] E_N(0, 0)$.

The energies $E_N(1, 0)$ and $E_N(0, 1)$ both refer to periodic systems in which the supercell has a net charge. To make these energies well defined, we must assume that the systems have been rendered electrically neutral by the introduction of a uniform background charge, as described in earlier papers [11,16,17]. The effect of the background charge densities is to make the zero-wavevector terms in the Coulomb energy finite rather than infinite, but these charge densities do not appear explicitly in any other way in either DFT or QMC.

In this way of doing the calculations, the interaction of the charged vacancies with their periodic images gives finite-size corrections ΔE to the total energy, which scale as L^{-1} , where the length L characterises the dimensions of the supercell. As is well known [11,16], these corrections can be quite accurately approximated by the formula $\Delta E \simeq \alpha q^2 / \epsilon_0 L$, where ϵ_0 is the static dielectric constant of the material, q is the net charge of the vacancy, and α is the appropriate Madelung constant. Using this formula, we can subtract off the leading finite-size corrections, and greatly accelerate the convergence with respect to supercell size. In applying this correction procedure in the present work, we take ϵ_0 for bulk MgO from experiment [20].

The present DFT calculations are performed using the VASP code [21] on a wide range of periodic cell sizes, as described above. These calculations allow us to determine the cell size needed to obtain converged results. The calculations employ the projector augmented wave method [22,23] for the interactions between the valence electrons and the ions, and the local density approximation for electronic exchange and correlation. In all the DFT calculations, the entire system is fully relaxed, so that the maximum force on any ionic core is less than 4×10^{-4} eV \AA^{-1} .

Detailed descriptions of VMC and DMC and of the CASINO code used for all the QMC calculations have been reported elsewhere [1,24]. Our trial wavefunctions Ψ_T have the usual Slater-Jastrow form $\Psi_T = D^\dagger D^\downarrow \exp(J)$,

where D^\dagger and D^\downarrow are Slater determinants of up- and down-spin single-electron orbitals, and $\exp(J)$ is the Jastrow factor describing correlations between electrons. The function J is a sum of parameterised one- and two-body terms, the latter being designed to satisfy the cusp conditions. The free parameters in J are determined by requiring that the variance of the local energy in VMC be as small as possible. The many-body wavefunction represents explicitly only valence electrons, whose interactions with the ionic cores are described by pseudopotentials. The Hartree-Fock pseudopotentials used here are the same as those used in our recent QMC work on bulk MgO [10]. The single particle orbitals have been taken from DFT-LDA calculations with the same pseudopotentials using the PWSCF code [18]. The basis set used for the representation of the single-particle orbitals in QMC is the recently described B-spline or blip-function basis [25], which is closely related to plane waves, but is computationally far more efficient for QMC. Since we cannot perform structural relaxations with QMC, the relaxed ionic positions used in our QMC calculations on the defective systems are taken from our DFT calculations.

In order to suppress statistical bias, QMC calculations need to be run with a large population of “walkers”, and this makes it efficient to run them on large parallel machines. The present calculations were performed on the HPCx machine at Daresbury using between 128 and 320 processors, with a target number of 640 walkers. One DMC step took about 7 seconds on 128 processors.

In Fig. 1 we display the value of Schottky energy calculated using DFT on various cell sizes, going up to 1024 atoms [19]. The results include the Coulomb correction mentioned above [16]. Two sets of calculations are reported in the figure: one performed by sampling the Brillouin Zone (BZ) at the Γ -point only, and the second using a $2 \times 2 \times 2$ Monkhorst-Pack [26] grid. The two sets of results become essentially indistinguishable for cells containing 128 atoms or more and converge very quickly to the value of 6.76 eV. The error in the Schottky energy obtained from calculations on cells containing only 54 atoms is somewhat less than 0.2 eV, but we note that cancellation of BZ errors makes the results obtained with 54 atoms and Γ -point only sampling already converged to within ~ 0.07 eV.

DMC calculations have been performed on cells containing 54 atoms, using a time step of 0.005 a.u. for over 50,000 steps. With this length of simulations, total energies for the perfect MgO crystal and the crystals with one Mg^{2+} or one O^{2-} vacancy were obtained with statistical errors of ~ 0.23 eV, ~ 0.32 eV and ~ 0.27 eV respectively. The value of the Schottky energy with the error bar obtained by combining the errors on the various components is 7.5 ± 0.53 eV. For completeness, we also report the value of the Schottky energy of 6.99 eV obtained using DFT-LDA with the same pseudopotentials used in the DMC calculations. Although there are

accurate experimental data for the migration energies of cation and anion vacancies in MgO, the Schottky energy itself is experimentally uncertain, with measured values spanning the range 4 – 7 eV [27]. Our QMC value is consistent with this, and also with earlier predictions for E_S from both DFT [11] and calculations based on interaction models [28,29], all of which give values in the range 6.5 – 7.5 eV.

These results demonstrate the technical feasibility of using high precision QMC calculations to study the energetics of defects in oxide materials. This is encouraging, because it suggests the possibility of using QMC to calculate the formation, association and migration energies of other kinds of defects, including impurities in oxide materials. In the present work, the QMC result for the Schottky energy agrees with the DFT predictions to within the QMC statistical error, but this is expected because DFT is known to give a good description of most properties of MgO. However, this will not be true of strongly correlated materials such as transition metal oxides, for which DFT predictions are often poor. We are currently attempting to extend our QMC calculations to the important oxide FeO.

A technical difficulty that is clear from the present work is that very long QMC runs are needed to reduce the statistical error on the defect energy to an acceptable level. This difficulty can be mitigated by improving the quality of the trial wavefunction. In the present case, we might do this by allowing the Jastrow factor to be different in the vacancy region. The use of recently developed methods for improving the scaling of the computer effort with system size [30–32] (so-called $O(N)$ QMC) will also help in future work. But the fundamental problem is that there is no cancellation of statistical noise on the large energies that are subtracted. Correlated sampling may perhaps help with this, but the solution may lie also in the close connection between $O(N)$ and embedding [33] that has already explored within tight-binding and DFT methods.

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[1] W. M. C. Foulkes, L. Mitaš, R. J. Needs, and G. Rajagopal, *Rev. Mod. Phys.* **73**, 33 (2001).
 [2] W.-K. Leung, R. J. Needs, G. Rajagopal, S. Itoh, and S. Ihara, *Phys. Rev. Lett.* **83**, 2351 (1999).
 [3] R. Q. Hood, P. R. C. Kent, R. J. Needs, and P. R. Bridgdon, *Phys. Rev. Lett.* **91**, 076403 (2003).

[4] S. B. Healy, C. Filippi, P. Kratzer, E. Penev, and M. Scheffler, *Phys. Rev. Lett.* **87**, 016105 (2001).
 [5] C. Filippi, S. B. Healy, P. Kratzer, E. Pehlke, and M. Scheffler, *Phys. Rev. Lett.* **89**, 166102 (2002).
 [6] J. C. Grossman, L. Mitaš, and K. Raghavachari, *Phys. Rev. Lett.* **75**, 3870 (1995).
 [7] R. J. Needs and M. D. Towler, *Int. J. Mod. Phys. B* **17**, 5425 (2003).
 [8] J.-W. Lee, L. Mitaš, and L. K. Wagner, unpublished.
 [9] See e.g., S. Massidda, M. Posternak, A. Baldereschi, and R. Resta, *Phys. Rev. Lett.* **82**, 430 (1999). For recent improved predictions using dynamical mean field theory, see e.g. S. Y. Savrasov and G. Kotliar, *Phys. Rev. Lett.* **90**, 056401 (2003).
 [10] D. Alfè, M. Alfredsson, J. P. Brodholt, M. J. Gillan, M. D. Towler, R. J. Needs, *Phys. Rev. B* submitted, cond-mat/0502510.
 [11] A. De Vita, M. J. Gillan, J. S. Lin, M. C. Payne, and I. Štich, L. J. Clarke, *Phys. Rev. B* **46** 12964 (1992).
 [12] A. M. Stoneham, *Theory of Defects in Solids*, Oxford University Press (2001).
 [13] N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).
 [14] *Computer Simulation of Solids*, edited by C. R. A. Catlow and W. C. Mackrodt (Springer-Verlag, Berlin, 1982).
 [15] J. H. Harding, *Rep. Prog. Phys.* **53**, 1403 (1990).
 [16] M. Leslie and M. J. Gillan, *J. Phys. C* **18**, 973 (1985).
 [17] G. Makov, M. C. Payne, *Phys. Rev. B* **51**, 4014 (1995).
 [18] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Gianozzi, <http://www.pwscf.org>.
 [19] We note in passing a technical problem that we encountered in the DFT calculations. The oxygen vacancy induces a gap state whose energy depends on the ionic positions. In some circumstances, partial occupation of this state can hinder the search for the ground state. However, for the relaxed system, the gap state lies well above the top of the valence band, and becomes completely unoccupied, so that the problem disappears.
 [20] G. Peckham, *Proc. Phys. Soc. London* **90**, 657 (1967).
 [21] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
 [22] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
 [23] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
 [24] R. J. Needs, M. D. Towler, N. D. Drummond, and P. R. C. Kent, ‘CASINO Version 1.7 User Manual’, University of Cambridge, Cambridge (2004).
 [25] D. Alfè and M. J. Gillan, *Phys. Rev. B* **70**, 161101(R) (2004).
 [26] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
 [27] W. C. Mackrodt, in *Computer Simulation of Solids*, eds. C. R. A. Catlow and W. C. Mackrodt (Springer-Verlag, Berlin 1982), p. 175.
 [28] C. R. A. Catlow, I. D. Faux and M. J. Norgett, *J. Phys. C: Solid State Phys.*, **9**, 419 (1976).
 [29] W. C. Mackrodt and R. F. Stewart, *J. Phys. C: Solid State Phys.*, **12**, 5015 (1979).
 [30] A. J. Williamson, R. Q. Hood, and J. C. Grossman, *Phys. Rev. Lett.* **87**, 246406 (2001).
 [31] S. Manten and A. Lüchow, *J. Chem. Phys.* **119**, 1307 (2003).

- [32] D. Alfè and M. Gillan, *J. Phys. Cond. Matt.*, **16**, L305 (2004).
[33] D. R. Bowler and M. J. Gillan, *Chem. Phys. Lett.* **355**, 306 (2002).

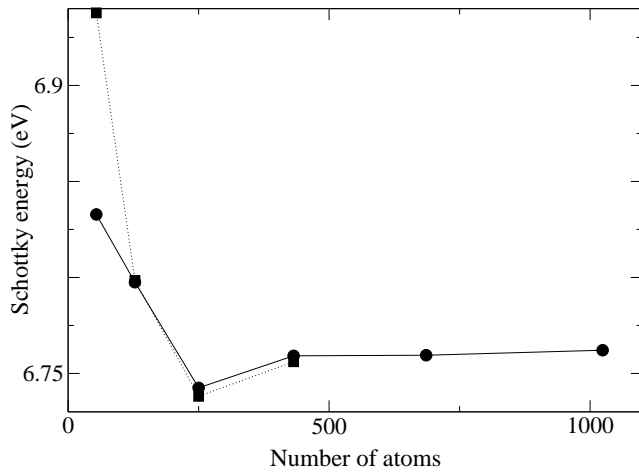


FIG. 1. Schottky vacancy formation energy (eV) in MgO calculated in the local density approximation of DFT for repeating cells containing different numbers of atoms. Filled circles connected by solid lines (filled squares connected by dotted lines) show results obtained with Γ -point ($2 \times 2 \times 2$ Monkhorst-Pack) Brillouin zone sampling.