

Quantum-mechanical Cluster Calculations and the Mott–Littleton Methodology

Robin W. Grimes and C. Richard A. Catlow*

Department of Chemistry, University of Keele, Staffordshire ST5 5BG

A. Marshall Stoneham

Theoretical Physics Division, AERE Harwell, Didcot, Oxfordshire OX11 0RA

We present results of quantum-mechanical cluster calculations of defects in ionic solids. We show how such calculations may be carried out with Mott–Littleton methodologies, and how the results of the two approaches may be compared. We present applications to defects in MgO and to noble-gas solute atoms in UO₂. We conclude with a study of the calculations of effective ionisation energies using cluster methods.

Although the Mott–Littleton methodology has been used with great success to investigate the energetics of defective materials, there are obviously many defect problems for which a solution of the Schrödinger equation is necessary. Broadly, a quantum-mechanical treatment is required when changes in electronic terms due to the creation of the defect cannot be incorporated into a parametrised effective potential. This will indeed be the case when defect formation includes a charge-transfer reaction, a transition to an excited state, the formation of certain colour centres or the electronic relaxation associated with a Jahn–Teller distortion.

For all the examples we have cited, the defect may be localised on a single lattice site or a small number of lattice sites. We may therefore model these defects by using an embedded cluster method. In this approach, the defect site and a number of surrounding ions are treated quantum-mechanically. The quantum cluster is then embedded in an outer region that is chosen so that it will approximate the variation in the electrostatic potential due to the surrounding lattice. A more detailed account of embedded quantum cluster methodologies is given in the previous article¹ and also by Grimes *et al.*² Unfortunately, quantum-mechanical techniques are computationally demanding and only a few ions can be incorporated in the quantum cluster. Therefore, cluster methods are restricted to calculating local responses to localised defects. As such, the effect of extensive ionic and electronic relaxations cannot be modelled. However, the response of a lattice to the inclusion of a defect is precisely what most Mott–Littleton-based codes are designed to model. The incentive for a concerted use of both methods is obvious. In fact, the advantage of using both methodologies to investigate individual defect problems extends beyond the simple partition of defect formation energies into electronic and relaxation terms. In this paper, we shall present a number of examples in which the two techniques have been used in a complementary fashion. Moreover, the results of one method may be used to illuminate, guide and validate the implementation of the other method. To illustrate this point, we shall apply both Mott–Littleton and embedded quantum cluster simulation techniques to the study of defects in MgO and UO₂. In the latter case we consider the noble gases which are generated as fission products when the material is used as a reactor fuel.

1. Definitions

The Mott–Littleton methodology is well documented in the present issue of this journal. It is therefore not necessary to discuss these techniques further in this article. However, it is necessary to clarify the definition of the various energy terms, when quantum cluster calculations are performed.

For a simple vacancy, the unrelaxed formation energy can be calculated from

$$\text{unrelaxed vacancy formation energy} = \text{energy of defective lattice} - \text{energy of perfect lattice} + \text{self-energy of displaced ion}.$$

The energy of the defective lattice is defined as the total energy of the quantum cluster that incorporates the vacancy site and the embedding point-charge array. The energy of the perfect lattice is the energy of the quantum cluster representing a specified number of perfect lattice ions and the appropriate point-charge array. The point-charge arrays surrounding the defective and perfect lattice clusters must be identical; only the quantum clusters may be different. The self-energy of the displaced ion is calculated by surrounding the displaced ion by a point-charge representation of the complete lattice, but with the contribution of the point-charge array to the displaced ion energy being subtracted out to yield a single ion energy [see ref. (2) for more discussion of this point].

Substitutional defect formation energies are calculated from

$$\text{substitutional defect formation energy} = \text{energy of defective lattice} - \text{energy of perfect lattice} + \text{self-energy of displaced ion} - \text{self-energy of substituted ion}.$$

The self-energy of the substituted ion is calculated in the same manner as the self-energy of the displaced ion. In this article, we shall only be concerned with simple vacancy and substitutional ion defects.

We shall begin discussing the complementary use of the two methodologies by addressing one of the most important problems in quantum-chemical calculations: the choice of basis set.

2. Basis-set Selection

Generally, in a single-determinantal Hartree–Fock calculation, the better the quality of the atomic basis sets, the closer the self-consistent calculation will be to the Hartree–Fock limit. However, the more extensive the basis set, the greater is the computational effort necessary to find the variational solutions to the Hartree–Fock equations. We must therefore find a balance between the basis-set quality and the computational cost of the calculation. A common way to tackle this problem is to use contracted basis functions that are optimised to atomic configurations. This is particularly useful for low-energy core orbitals which are usually only slightly perturbed by molecular forces. Valence orbitals require greater flexibility since these are significantly modified through molecular bonding interactions.

In this study, we have chosen three types of basis set, all of which comprise linear combinations of Gaussian orbitals. The lowest-quality basis, STONG, comprises fixed combinations of n Gaussian orbitals, the linear coefficients having been chosen by fitting the overall orbital shape to an atomic Slater-type orbital (STO). This basis allows no flexibility in the valence orbitals. The intermediate quality basis, SV3-21G, splits the valence orbital (SV) that was previously represented by three Gaussian orbitals into two independent orbitals, one of which is represented by a fixed sum of two Gaussians, the other by a single Gaussian. In the highest-quality basis, TZV, the valence orbitals are

Table 1. Oxygen vacancy energy in MgO calculated with various combinations of basis sets and a small cluster geometry

basis for oxygen ion	basis for magnesium ion	energy/eV
TZV	TZV	42.064
TZV	SV3-21G	42.309
SV6-21G	SV6-21G	50.472
SV3-21G	SV3-21G	50.607
STO 6G	STO 6G	65.269
STO 3G	STO 3G	65.980

Table 2. Total energies calculated from embedded quantum cluster method and their dependence on basis for a range of anions (all energies in hartree)

quantum-mechanically modelled cluster size			
	anion and (100) Mg ions	anion only	defect-formation energy
		F ⁻	
TZV	134.8957	156.7986	0.7424
SV3-21G	134.3601	156.1316	0.6109
difference	0.5356	0.6670	
		Cl ⁻	
TZV	1703.1695	516.8601	0.5299
SV3-21G	1700.9893	514.6772	0.5273
difference	2.1801	2.1829	

once again split, usually into three independent orbitals. However, the split orbitals are also normalised in a manner that provides a reasonable representation of the atomic valence orbitals.

In table 1, we present calculations of unrelaxed oxygen vacancy energies carried out using different choices of basis set. [For further details of the calculational methods see ref. (2).] The important point to note in these results is that as the quality of the basis is improved from STO3G to TZV, the defect-formation energy decreases and approaches the value calculated using the Mott-Littleton method (*i.e.* 40.765 eV). Thus, in the case of this simple defect, we are able to use the Mott-Littleton simulations to decide on the necessary quality of the basis functions to be used in a parallel quantum cluster calculation. Closer inspection of table 1 shows that we require a TZV basis for oxygen but only an SV3-21G basis for magnesium. This is due to the more diffuse nature of the anion electron density and its high polarisability.

The use of a defect-formation energy to indicate the quality of basis required to calculate reliable energies, as in table 1, can sometimes be misleading. Consider in table 2 the examples of the formation energy of the ions fluoride and chloride substituted at oxygen sites. Both TZV and SV3-21G basis are used for fluorine and chlorine, but for magnesium only the SV3-21G basis is employed. It is apparent that the basis sets give rise to very similar formation energies for chlorine but rather different values for fluorine. We might be tempted to conclude that, although the higher quality TZV basis is required on fluorine, SV3-21G suffices for chlorine. The result does indeed indicate that a TZV basis is needed on fluorine, but the converse result for chlorine is invalid. This can be

seen by looking at the total energies for the individual chlorine defect clusters (ClMg_6 and Cl in point-charge arrays). We see a large decrease in total energy as the basis is improved, showing that the better quality basis still has a significant effect on the stability of the system. However, the decrease is equally large for both chlorine clusters and the basis-set effect cancels out in the final formation energy. In other words, the invariance of the defect-formation energy with increasing basis set is a necessary but not sufficient condition that the lower-quality basis can be employed.

3. Electronic Polarisation within a Self-consistent Calculation

Once adequate basis functions have been chosen for anions and cations, we may proceed with the defect-energy calculations. The first defects we consider are the simple oxygen and magnesium vacancies in MgO . The quantum clusters consist of the defect site and first-nearest-neighbour ions only [see fig. 1(a)]. In table 3 we report the values for unrelaxed lattice geometries. The values for the oxygen vacancy (V_{O}^{\bullet}) calculated by Mott-Littleton and embedded cluster methods are very close, whilst formation energy values for the magnesium vacancy (V_{Mg}^{\bullet}) differ by 5.6 eV. This discrepancy is due largely to the electronic polarisation of the nearest-neighbour oxygen ions around the magnesium vacancy. The embedded cluster technique includes electronic polarisation by virtue of its self-consistent methodology, whereas in the Mott-Littleton method electronic polarisation is included only if we incorporate a suitably parametrised model. In these Mott-Littleton calculations, we will use the shell model of Dick and Overhauser³ to reproduce the effect of electronic polarisation.

In the third column of table 3, the Mott-Littleton calculations are repeated with electronic polarisation included on ions that in the embedded cluster method are within the quantum cluster, *i.e.* on the nearest-neighbour ions to the defect. Values for defects centred at oxygen sites are not changed since we do not consider cations to be polarisable and consequently, no ions in the quantum cluster will polarise. Justification of this is given by the fact that the calculated oxygen vacancy energies from the quantum cluster simulations agree so well with the Mott-Littleton values.

The inclusion of electronic polarisation of nearest-neighbour ions in the Mott-Littleton calculation of the magnesium vacancy results in a decrease in this unrelaxed geometry formation energy of 9.9 eV. The Mott-Littleton value is now 4.3 eV lower than the embedded cluster value. Although the embedded cluster calculation includes electronic polarisation effects, the extent to which it is able to model these terms is limited by the basis functions used. Using the small quantum cluster [fig. 1(a)] and the central atomic basis functions, the oxygen ions are able to model the polarisation effects only partially.

A better description of polarisation is gained by using the larger cluster depicted in fig. 1(b). The basis functions of the outer shell of magnesium ions are now available to participate in modelling the polarisation effects. Using this cluster, the embedded cluster method calculates a magnesium vacancy formation energy of 34.15 eV. If second-nearest-neighbour magnesium ions were included in the quantum cluster, the embedded quantum-cluster magnesium vacancy energy would undoubtedly be even closer to the value calculated by the Mott-Littleton methodology. This is a particularly important result since it suggests that the shell model for polarisation parametrised by fitting to dielectric data is consistent with a self-consistent-field quantum cluster model.

Formation energies for a number of substitutional ions in MgO are also presented in table 3. Although there is generally good agreement between values calculated by the different methods, discrepancies of up to 10% are sometimes apparent. This is probably due to uncertainties in the short-range interatomic potentials used in the Mott-Littleton method. We can be confident in the quality of the bulk lattice MgO potentials since they have been fitted to a large range of experimental data [see ref.

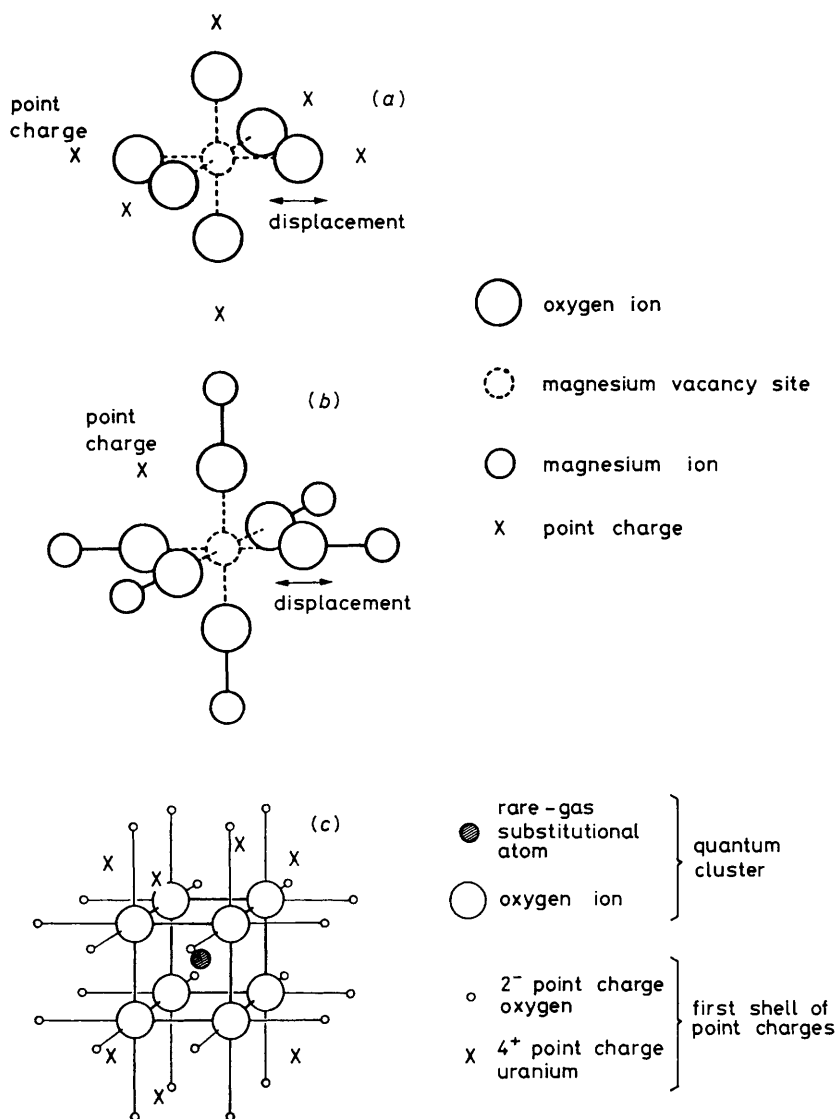


Fig. 1. Embedded quantum clusters used in defect-formation energy calculations. (a) MgO small cluster. (b) MgO large cluster. (c) UO₂-centred cluster.

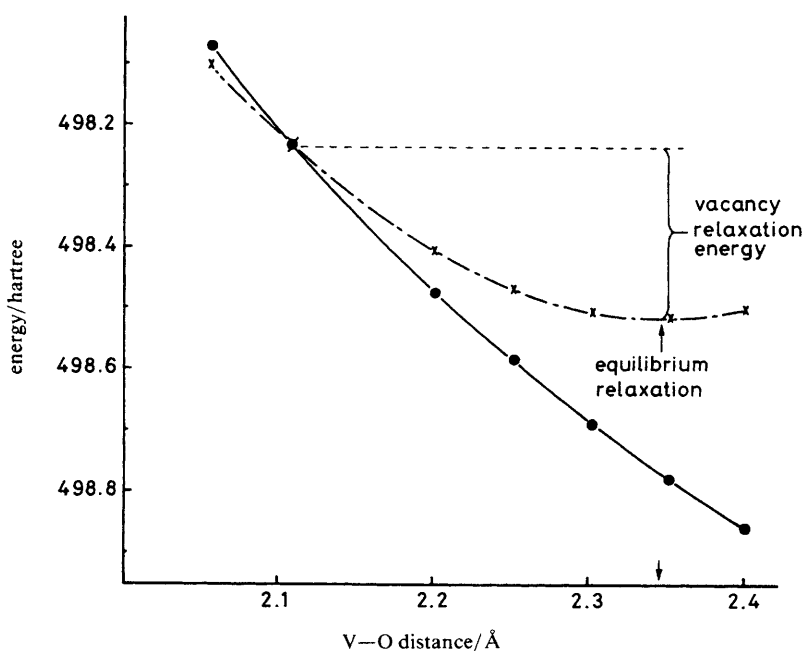
(4)]. However, the short-range potentials involving substitutional ions have been calculated using electron-gas methods and made consistent with empirical lattice potentials by the method developed by Butler *et al.*⁵ [see also ref. (2)]. This is the most widely used procedure when calculations on impurities are performed using Mott-Littleton methods and empirical potentials.

4. Ionic Relaxation

In the Introduction, we remarked that an embedded cluster method can only be used to calculate local responses to localised defects. This problem is particularly acute when

Table 3. Vacancy and substitutional defect-formation energies in MgO (all energies in eV)

	embedded quantum cluster with unrelaxed nuclear positions	Mott-Littleton unrelaxed	Mott-Littleton allowing (100) shell relaxation
V_{Mg}''	35.167	40.765	30.865
V_{O}''	40.558	40.765	40.765
Li_{Mg}'	17.564	17.540	14.598
Al_{Mg}'	20.274	22.964	19.053
F_{O}'	18.873	19.117	19.117
Cl_{O}'	26.663	25.655	25.655

**Fig. 2.** Calculated relaxation of nearest-neighbour oxygen ions around a magnesium vacancy using embedded quantum cluster methodology. Total energy from GAMESS: ●, using small q.m. cluster; ×, using large q.m. cluster.

we wish to calculate lattice relaxation around the defect. In this section we shall demonstrate the point by studying relaxations around a magnesium vacancy in MgO.

Consider the relaxation of first-nearest-neighbour ions around a magnesium vacancy. If we use the quantum cluster shown in fig. 1(a) the ions relax out to an unphysical extent. This is illustrated in fig. 2. The quantum-mechanically treated first-nearest-neighbour (100) ions are able to relax away from the defect site towards the point ions because the point ions offer no short-range repulsive interaction. If we treat the (200) shell quantum-mechanically [see fig. 2(b)] the nearest-neighbour ions relax outwards by only 0.20 Å, a much more physically realistic displacement. Equivalent Mott-Littleton simulations yield relaxation displacements of 0.22 Å [see ref. (2)].

If we are to model relaxation effects explicitly it is obvious that account must be taken of short-range repulsive interactions. Since it would be impossible to model

Table 4. Magnesium vacancy formation energies (eV)

calculations with electronic polarisation only	
quantum cluster-formation energy with no continuum contribution	34.15
quantum cluster-formation energy with continuum relaxation energy	28.89
Mott-Littleton relaxed formation energy ^a	28.63
calculations with displacement + electronic polarisation	
quantum cluster-formation energy with nearest-neighbour ionic displacement but no continuum contribution	31.11
relaxed nearest-neighbour quantum cluster formation with continuum relaxation energy	22.43
Mott-Littleton relaxed formation energy ^a	24.00

^a region I = 4.1 lattice units.

sufficient ions quantum-mechanically, it would seem appropriate to interface a quantum cluster method with the current Mott-Littleton methodology. This work is being pursued by Harding *et al.*⁶ [see also ref. (1)]. In the present context, however, we are able to make use of the original Mott-Littleton continuum relationship to calculate the response of the lattice to the magnesium vacancy.

The relaxation energy $E(R)$ around a cavity of radius R is given by

$$E(R) = e^2/2R(1 - 1/\epsilon)$$

where e is the effective charge of the defect site, and ϵ is the static dielectric constant ϵ_0 (assuming that both core and shell relaxation are being modelled) or ϵ_∞ (if only shell displacements are allowed). If the nearest-neighbour lattice distance is a_0 , then considering that the quantum cluster includes the nearest-neighbour ions, the value of R will be $\sqrt{(2a_0)}$ if both core and shells are relaxed but $\sqrt{(3a_0)}$ if shells only are relaxed. This latter value of R is larger as the second-nearest-neighbour ions are cations and are not considered to be polarisable.

The results of using the continuum model in conjunction with the quantum cluster are given in table 4. The close agreement to values calculated using the current Mott-Littleton methodology shows that for certain special cases, we can use this relatively simple procedure to derive useful energies. Moreover, it demonstrates how, at even relatively small interatomic separations, the original Mott-Littleton relationship can come surprisingly close to describing the ionic and electronic responses of an ionic crystal to the inclusion of defects.

5. Basis-set Superposition Errors

In section 2 it was shown that in the embedded cluster calculation, the atomic basis set for oxygen was not able to model the electronic polarisation of an oxygen ion around a magnesium vacancy. This resulted in the oxygen ion using basis functions centred on the magnesium sites. Problems due to the inadequacy of basis sets can be very severe and, in molecular configurations, may cause significant errors when differences in total cluster energies are used; such errors are known as basis-set superposition errors.

Generally, in a molecular configuration, an atom has available to it its own atomic basis and also the basis functions associated with all the other atomic species. If it is energetically favourable, the variational calculation will incorporate contributions from basis functions on other centres to lower the Hartree-Fock energies of the individual components. This effect leads to an error if we wish to calculate the energy associated with forming bonds since the initial energies of the atomic species are effectively changed.

Table 5. Basis-set superposition error associated with vacancy and substitutional defects in MgO calculated using embedded quantum cluster methodology (all energies in eV)

	uncorrected defect- formation energies	values corrected for BSSE	BSSE energies
V_{Mg}''	36.688	35.167	-1.521
V_{O}''	42.309	40.558	-1.751
Li_{Mg}'	17.670	17.564	-0.106
Na_{Mg}'	20.086	20.274	0.188
Al_{Mg}'	-23.129	-23.201	-0.072
F_{O}'	20.203	18.872	-1.331
Cl_{O}'	25.719	26.663	0.944

If E_{AB} is defined to be the energy of a molecule comprised of two atoms A and B, and if E_{A} , E_{B} are energies of the individual components, the energy to form the bond, ΔE_{AB} , is given by

$$\Delta E_{\text{AB}} + \Delta E_{\text{A}} + \Delta E_{\text{B}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$$

where ΔE_{A} and ΔE_{B} , the basis-set superposition energies are defined by

$$\Delta E_{\text{A}} = E_{\text{A}}(\text{molecule}) - E_{\text{A}}$$

where $E_{\text{A}}(\text{molecule})$ is the energy of atom A calculated with the additional basis of atom B centred at the position the atom B will occupy in the molecule but without either the nucleus or the electrons of atom B. This manner of calculating the error is known as the functional counterpoise method.⁷

It has been suggested⁸ that the functional counterpoise method provides an overestimate of the basis-set superposition error, since orbitals made available for the correction calculation will be, in the complete cluster, fully occupied. Therefore, as the Pauli principle will restrict the use by atom A of core orbitals from atom B they should not be made available in the correction calculation.⁸ In accordance with this, we shall use the virtual-only functional counterpoise method⁹ in which only virtual orbitals are made available to the correction calculation. It has recently been shown by Grimes *et al.*² that using only the virtual orbitals for the basis-set superposition determination is particularly important in embedded cluster calculations where the large electrostatic fields present in solid oxides can cause spurious charge transfer to superposition basis orbitals and thereby obscure the real superposition effects.

In table 5, we present the results of calculations of the basis-set superposition error for a range of vacancy and substitutional ions in MgO. The superposition energies can cause changes in defect formation energies from as little as 0.3% up to as much as 6.6%. However, in all cases the effect is not great enough to change qualitative conclusions concerning relative defect energies.

If we now consider the superposition energies associated with calculations of solution energies of noble-gas atoms at uranium vacancy sites in UO_2 (see table 6), we find that the errors represent a much greater percentage of the absolute solution energy. This is not only because the absolute values of these solution energies are smaller than the defect formation energies were in MgO, but also because of the large size of the gas atoms compared to their solution site. This size difference causes significant changes to the valence-orbital shapes and therefore the orbital flexibility provided by orbitals on other centres is exploited.

If we use Mott-Littleton methodology to provide relaxed nearest-neighbour coordinates around the solute atoms, the basis-set superposition energy is reduced by a factor

Table 6. Basis-set superposition errors associated with fission gases in UO_2 (all energies in eV)

	Mott-Littleton solution energies	BSSE unrelaxed	BSSE relaxed
Ne	2.31	2.14	0.35
Ar	4.08	3.63	0.58
Kr	5.87	4.39	1.12
Xe	7.21	8.47	2.18

of at least four. The relaxed coordinate solute site is significantly larger than the unrelaxed uranium vacancy site so that the solute atom wavefunction has to undergo less deformation when occupying this site. Consequently, the superposition energy is less (see table 6).

In modelling defect energies using embedded quantum cluster methods, superposition energies will be reduced when we use relaxed defect configurations. Generally then, in using a combination of Mott-Littleton and quantum cluster methods, we should first use the Mott-Littleton method to provide a relaxed coordinate environment in which to carry out the quantum cluster calculation.

6. Ionisation Energies in the Solid State

In this final section of the paper we investigate a problem where the use of embedded quantum cluster methods is essential; we shall consider the calculation of ionisation energies for localised excitations in solids.

In the gas phase, we can define the ionisation energy (I_g) to be the energy required to remove an electron from an atom or ion in charge state $(n-1)$ and to place the electron at infinity. When the same ion is in a solid, the energy for the same process (I_s) includes (i) a contribution due to the electrostatic field of the other ions in the solid, that is the Madelung energy, E_M , of an electron at the ion site and (ii) a contribution from the polarisation energy. The latter arise because the solid responds to the change in charge state in the same way as it would to the formation of any defect. Thus we may define ΔE_p as the change in polarisation due to a change in the charge state of an ion. By definition E_p is zero for a lattice ion in its usual charge state at its usual lattice site.

We may now write an expression for I_s including the quantity I_{eff} , which is the effective solid-state ionisation energy:

$$I_s = I_{\text{eff}}^n + E_M + \Delta E_p.$$

The value of I_{eff} will be considerably different from I_s because E_M or ΔE_p are large terms. This is most readily shown by the O^{2-} ion which is a well defined species in the solid state but does not exist as a gas-phase ion.

As we have already seen, lattice relaxations and hence ΔE_p must be calculated using Mott-Littleton methodology. To calculate I_{eff} , however, we must employ a quantum-mechanical method. As an example let us consider the energy to remove an electron from an O^{2-} ion in MgO . To calculate I_{eff} we can use the embedded cluster method in which the quantum cluster is either a single oxygen ion or an oxygen ion surrounded by its six nearest-neighbour magnesium ions (OMg_6). In each case, the appropriate embedding ions will provide the Madelung potentials and electrostatic fields on all the cluster ions that those ions would experience in a bulk solid. The calculation of I_{eff} involves taking the difference between total cluster energies. In the case of the single-atom

Table 7. Ionisation energies of xenon in the gas phase and at a pre-existing uranium vacancy site in UO_2 (all energies in eV)

	$\text{Xe}^0 \rightarrow \text{Xe}^+$	$\text{Xe}^+ \rightarrow \text{Xe}^{2+}$
experimental gas-phase value	12.13	21.21
calculated gas-phase value	11.66	20.03
single-atom clustered ^a calculation in UO_2	11.96	20.13
(XeO_8) cluster ^a calculation in UO_2	14.20 ^b	20.99 ^b
(XeO_8) cluster ^a calculation in UO_2	12.04	20.14

^a The nearest-neighbour ions or point charges to the xenon ion have been relaxed. ^b These values include an energy contribution ΔE_p from the polarisation of the nearest-neighbour oxygen ions.

cluster this is between $[\text{O}]^{2-}$ and $[\text{O}]^-$ (including the point-charge arrays); in the case of the larger cluster, it is between the $[\text{OMg}_6]^{10+}$ and $[\text{OMg}_6]^{11+}$ clusters. From the difference in energy, the Madelung energy, E_M , must also be subtracted. In the case of MgO , E_M at an oxygen site is 23.88 eV. The value of ΔE_p for these cluster calculations is zero since we have not included ionic displacements and magnesium ions can be regarded as non-polarisable.

The value of I_{eff} calculated using the single-atom cluster is -11.67 eV. The larger cluster yields a value of -14.55 eV. The negative values indicate that the energy to take an electron from an O^{2-} ion after the positive Madelung contribution has been subtracted, is favourable. As is well known, it is the Madelung energy that contains the second negative charge at the oxygen site; the I_{eff} contribution to I_s repels the second negative charge.

The (OMg_6) cluster value for I_{eff} is 2.88 eV larger than the single-ion value. The six nearest-neighbour magnesium ions confine the oxygen wave function to a smaller atomic volume, thereby further repelling the second negative charge.

In order to determine a final value for the effective second electron affinity of oxygen in MgO , we wish to use larger clusters that incorporate for example second-nearest-neighbour ions. Also, we have neglected correlation effects that will stabilise the second negative charge and reduce I_{eff} . However, these calculations show how the embedded quantum cluster method can be used to calculate electron affinities and illustrates the relative simplicity of this application.

For the second example of ionisation energies we shall consider the first two ionisation processes of a xenon atom situated at a pre-existing uranium vacancy site in UO_2 . These values are of particular interest in fission-product studies since they are needed to determine the charge state of xenon in the UO_2 host and hence its stability as a solute ion.

Initially, we calculated gas-phase ionisation energies to compare with experimental results. The similarity of experimental and calculated values (see table 7) shows that the basis set for xenon used in these calculations (due to Huzinaga *et al.* and split 3-21 for 5s and 5p and 5-221 for 5d) is adequate for ionisation calculations. The discrepancies between calculated and experimental results are due to the neglect in these calculations of many-electron (particularly correlation) effects. However, the method will still be able to supply information concerning the effect of the crystal environment on the ionisation energy.

Bulk xenon ionisation energies (I_s) were calculated in an equivalent manner to the example of oxygen in MgO. The Madelung energy was subtracted and values are presented in table 7. The nearest-neighbour ions (or point charges) to the xenon ion were relaxed with respect to a neutral defect atom using the Mott-Littleton methodology since the ionisation energies we wish to consider are with respect to a stable fission-gas atom in UO_2 .

The point-charge representation of the crystal environment causes only a small increase in the ionisation energies of xenon. However, the inclusion of quantum-mechanically treated nearest-neighbour oxygen ions causes a marked increase in energies (see table 7), since oxygen ions will polarise differently in the two charge states of xenon, thereby providing a ΔE_p energy term as discussed earlier in this section. This contribution can be calculated using the Mott-Littleton methodology and subtracted from the ionisation values. Results of this process are also presented in table 7. It can be seen that in fact, the use of the larger (XeO_8) cluster has little effect on ionisation energies in contrast to the effect a large cluster had on the oxygen ionisation energy in MgO. The more localised wave function of the Xe atom renders the gas-phase ionisation energies more appropriate for the solid-state environment.

Conclusions

The calculations reported in this paper show that realistic quantum cluster calculations can be performed in order to study defects in insulating solids; but that such calculations can be made more effective when combined with Mott-Littleton treatments of lattice relaxation. Cluster methods can also play a valuable role in calculating effective ionisation energies in ionic solids.

R.W.G. thanks the Theoretical Physics Division, AERE, for financial support.

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Paper 8/04379E; Received 2nd November, 1988