Ab initio Cluster Calculations of Defects in Solids [and Discussion]

R. Jones and P. C. H. Mitchell

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Ab initio cluster calculations of defects in solids

By R. Jones

Department of Physics, University of Exeter, Exeter EX4 4QL, U.K.

A method based on local density functional theory is described which leads to the rapid determination of the structure, vibrational and electronic properties of clusters as large as 100–150 atoms. The technique is particularly suitable for molecular solids, covalently bonded materials where the clusters are terminated by hydrogen, and to ionic systems where the termination consists of a set of distributed charges. The strengths and weaknesses of the method are detailed together with an application to the interstitial carbon–oxygen complex in silicon where oxygen is found to be over-coordinated. The good agreement obtained for the vibrational modes of the complex lends support to the unusual structure found.

1. Introduction

The determination of the properties of defects in solids – and I have in mind complicated defects like dislocations and impurity aggregates – poses severe problems. First, one needs to be able to describe correctly the charge distribution around each atom and to evaluate the force acting on it. Thus a method of solving the many body Schrödinger equation is required. The two standard methods: Hartree–Fock (HF) and local density functional (LDF) theories (Lundqvist & March 1986; Ihm 1988) are not devoid of approximations and assumptions but they have been found to be particularly useful for ground state molecular and crystalline structures. Each is a variational procedure with HF theory assuming the wavefunction, which is dependent on the coordinates of all the electrons, as the variational variable whereas LDF theory takes it to be the charge density: a function of just three coordinates (in the spin-polarized version, the variational variables include the magnetization density). Both theories can be written in terms of single particle Schrödinger equations with the potential acting on a electron arising from an effective field due to all the others. Thus both require a self-consistent equation to be solved. However, there are important differences; especially in the treatment of exchange and correlation. HF theory ignores the latter and its inclusion via say Möller–Plesset perturbation theory is unwieldy. For metallic systems correlation is essential and for this reason HF methods have primarily been used in insulators. LDF theory includes a correlation term derived from the homogeneous electron gas but its utility in multi-atomic systems where the charge density varies rapidly is well proven. The exchange energy in HF theory is a four-centre integral and its evaluation requires the computation of $O(N^4)$ integrals, where N is the basis size. This is to be contrasted with LDF theory whose exchange-correlation energy is an integral of a function of the electron density $n(\boldsymbol{r})$ and its evaluation requires $O(N^2M)$ computations where M is the number of points or operations involved in estimating this integral. In many applications this scales as N or the cluster size. We should say that this applies to

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clusters of about 100 atoms, where typically each basis function has some overlap with almost all the others. Thus we expect LDF theory to be about N times faster than HF and for typical values of N around 500 to 1000, this makes HF theory slower for large systems. Nevertheless, the latter theory has been used with some success for large systems (Maric *et al*. 1989; Nada *et al*. 1990).

A second reason for preferring LDF over HF theory is that for many purposes it is only the valence electrons that are important in chemical bonding. The development of pseudopotentials (Bachelet *et al*. 1982; Yin & Cohen 1982) eliminating the need to include core electrons has been successfully accomplished in the case of LDF theory. The total electron density is composed of two parts: a core density which is the sum of contributions from different atomic cores and is large near each atom but falls off rapidly to zero, and the valence charge density which although varying rapidly near the core (because of the constraints imposed by orthogonalization) is relatively smooth around the centres of chemical bonds. The pseudo-atoms have no core states and thus their 'valence' electrons experience a repulsive potential leading to a small and slowly varying charge density in the core region. In the frozen-core approximation, the exchange-correlation energy for the pseudo-atom is then determined by this valence charge density alone. This is of great significance for it is a difficult task to construct a basis set for both the core and valence wave-functions as each of these quantities has a different domain of importance and scale of variation. The result is that it is of no greater difficulty in treating say GeO_2 than SiO_2.

The nature of the exchange energy in HF theory involving the product of four orbital functions some of which may be core ones has made it more difficult to develop reliable pseudopotentials. Thus the most efficient way of treating defects in semiconductors may well be based on LDF theory incorporating pseudopotentials and thereby eliminating core electrons. However, some quantities dependent on the core wave-functions, such as chemical shifts, may not then be calculable. This is not always the case as Van de Walle (1990) finds good agreement for the relative hyperfine and super-hyperfine parameters (quantities depending on the wave-function near the nucleus) for H in Si.

Finally, one requires an efficient method of solving the Schrödinger equation and, in addition, it is essential to be able to calculate the forces acting on individual atoms and allow the positions of these to adjust until an equilibrium structure is found.

There appear to be three methods: first, the Green function method (Baraff & Schlüter 1983) which is the most rigorous one for point defects. Much effort is expended on the evaluation of the host lattice Green function, more elements of which are required when the size of the defect increases. Second, the supercell method which uses a basis of plane-waves together with the molecular dynamical method of Car & Parrinello (1984) and seems ideal for many problems. There are difficulties for certain elements, e.g. O, F and transition ones, due to the lack of p or d core electrons as this makes the valence wave-functions vary rapidly near the cores with the consequence that one requires an extremely large number of plane-waves. A second difficulty is that for certain defects, e.g. partial dislocations in semiconductors, it is necessary for topological reasons to construct unit cells containing dislocation dipoles. The present limitation of unit cell size causes the dislocations to lie unsatisfactorily close together. In other systems such as zeolites or proteins where the unit cells contain hundreds or even thousands of atoms it may not be easy to construct a sufficiently small cell for computational purposes. The third method is based on atomic clusters. The essential problem here is to passivate the surface of the cluster in such a way that properties of the inner part are insensitive to the termination. For non-metallic solids this requires a surface without gap states whose charging would draw charge from the inner part of the cluster. This would affect the properties of the inner atoms. A practical way of doing this is to passivate surface dangling bonds of covalently bonded materials with hydrogen. Moreover it is important to choose a short H-surface length as this depresses the H-bonding states below the bulk valence band top and elevates the H-antibonding states to above the bulk conduction band. However, since the host feels a repulsive potential from the surface H atoms, its valence and conduction bands are also depressed and elevated respectively resulting in an increased band gap. This effect of H in increasing the band gap is realized in a-Si:H and, possibly, porous Si. However, it seems that this band gap widening does not significantly affect structural or vibrational properties, although it does lead to defect levels lying deeper in the gap than observed. It is known that small H-terminated molecules have structures and vibratory modes close to those of the bulk. For example, neopentane C_5H_{12} has a bond length within 1% of diamond whereas disiloxane, $(SiH_3)_2O$, has an Si–O length of 0.1634 nm and vibratory modes at 1107 and 606 cm^{-1}, which lie close to those of interstitial oxygen in Si: 0.16 nm, 1136 and 515 cm^{-1} (Stavola 1984). The termination must be different for ionic systems and here a distribution of fixed charges has been used to surround the cluster.

I shall describe the cluster method that I have developed in more detail in the next section. Note here that several other workers have also developed cluster LDF methods (Pederson & Jackson 1990) but not incorporating pseudopotentials. I shall give what I see as the strengths and weaknesses of the method in §3 and an application in §4. Before this I make some remarks on approximate methods. These are like CNDO, MNDO, PRDDO or the tight binding scheme where approximations to the HF or LDF theories are made at the outset. Very often these include empirical information and, provided that the bonding is properly described, give these methods a wide domain of applicability and usefulness. In particular they can give stretch frequencies *systematically* higher than those observed and this is a very useful result.

2. The LDF cluster method

The total energy of the cluster is given by the minimum of

$$E = E_{\mathrm{ke}} + E_{\mathrm{e\text{-}p}} + E_{\mathrm{H}} + E_{\mathrm{xc}} + E_{\mathrm{i\text{-}i}}.$$

Here E_{ke}, $E_{\mathrm{e\text{-}p}}$, E_{H}, E_{xc}, and $E_{\mathrm{i\text{-}i}}$ are the kinetic, electron–pseudopotential, Hartree, exchange-correlation and ion–ion energies respectively. The charge density $n(\boldsymbol{r})$ is written in terms of the wave-functions, $\psi_\lambda(\boldsymbol{r})$, of occupied states, each of which is expanded in a basis set $\phi_i(\boldsymbol{r})$ of localized orbitals.

It is then necessary to vary the coefficients in the wave-functions in order to minimize E subject to the usual constraint that the total number of electrons is fixed. This is achieved by writing Euler–Lagrange equations for these coefficients. These equations can be cast in a matrix form involving integrals over the basis functions. We have, for the λ wave-function:

$$\psi_\lambda(\boldsymbol{r}) = \sum_i c_i^\lambda \phi_i(\boldsymbol{r}),$$

and the set of c_i^λ which minimize E, subject to the constraint that the cluster contains the correct number of electrons, satisfy (Jones & Sayyash 1986):

$$\sum_j (KE_{i,j}+V^p_{i,j}+V^H_{i,j}+\mu_{i,j}-E_\lambda S_{i,j})\,c_j^\lambda = 0.$$

Here $KE_{i,j}$, $V^p_{i,j}$, $V^H_{i,j}$, $\mu_{i,j}$, and S_{ij} are the matrix elements for the kinetic, pseudopotential, Hartree and exchange-correlation potentials and overlap respectively.

Gaussian basis functions have the advantage that all the required integrals can be analytically performed. It is trivial to evaluate the integrals involving the kinetic energy, and the pseudopotential; especially if one uses those given by Bachelet *et al.* (1982). This leaves the two troublesome terms: the Hartree energy, E_H, and the exchange-correlation energy, E_xc where

$$E_\mathrm{H} = \frac{1}{2}\int \frac{n(\boldsymbol{r}_1)\,n(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$$

and

$$E_\mathrm{xc} = \int \epsilon_\mathrm{xc}(n)\,n\,\mathrm{d}\boldsymbol{r},$$

where ϵ_xc is the exchange-correlation energy density.

For large systems it is not possible to treat these terms exactly. Consequently some approximation must be used. It is important that the approximations used in evaluating E_H and E_xc are consistent with those in the Hartree and exchange-correlation potentials otherwise the self-consistent density would not be the one that minimizes the total energy.

To achieve this we replace E_H and E_xc with approximate expressions $\tilde{E}_\mathrm{H}$ and $\tilde{E}_\mathrm{xc}$ (Jones & Sayyash 1986; Jones 1988). Here

$$\tilde{E}_\mathrm{H} = \int \frac{n(\boldsymbol{r}_1)\,\tilde{n}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2 - \frac{1}{2}\int \frac{\tilde{n}(\boldsymbol{r}_1)\,\tilde{n}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$$

and

$$\tilde{E}_\mathrm{xc} = \int \epsilon_\mathrm{xc}(\tilde{n})\,\tilde{n}\,\mathrm{d}\boldsymbol{r}.$$

It is clear that these expressions are exact when $\tilde{n}=n$.

We define the approximate density $\tilde{n}(\boldsymbol{r})$ in terms of basis functions $g_k(\boldsymbol{r})$ by

$$\tilde{n}(\boldsymbol{r}) = \sum_k c_k\,g_k(\boldsymbol{r}).$$

It is most sensible to choose the coefficients c_k by requiring the difference between $\tilde{E}_\mathrm{H}$ and E_H to be as small as possible (Dunlap *et al.* 1979). This difference can be written as

$$\frac{1}{2}\int \frac{(n(\boldsymbol{r}_1)-\tilde{n}(\boldsymbol{r}_1))(n(\boldsymbol{r}_2)-\tilde{n}(\boldsymbol{r}_2))}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2.$$

Then the coefficients c_k are chosen to minimize this expression. In practice we choose some g_k to be the functions $(1-\frac{2}{3}a_k(\boldsymbol{r}-\boldsymbol{R}_k)^2)\exp(-a_k(\boldsymbol{r}-\boldsymbol{R}_k)^2)$ and others just s-gaussians centred at $\boldsymbol{R}_k$. The point about the first set is that they give a potential which is just $(2\pi/(3a_k))\exp(-a_k(\boldsymbol{r}-\boldsymbol{R}_k)^2)$ and thus the matrix elements $\tilde{V}^H_{i,j}$ are trivial to compute (Jones 1989). Since, however, each of the first set of functions integrates to zero it is essential to include some functions of the second type. The sites $\boldsymbol{R}_k$ are taken to lie at both atomic and bond centres.

To evaluate $\tilde{E}_{\mathrm{xc}}$ we use

$$\tilde{E}_{\mathrm{xc}} = \sum_k c_k \int g_k(\boldsymbol{r})\, \epsilon_{\mathrm{xc}}(\tilde{n})\, \mathrm{d}\boldsymbol{r}$$

and estimate the integrals using the first few moments of $\tilde{n}$ over g_k. We do not need to use the same coefficients c_k and functions g_k for $\tilde{n}$ and instead use a least squares fit to n using simple gaussian functions.

The key remark is then that the Euler–Lagrange equations for the wave-function are then derived from minimising this approximate energy expression. Thus the self-consistent density is necessarily the one giving the lowest energy $\tilde{E}$. This would not be the case if one used different approximations to evaluate say E_{H} and the matrix elements of the electrostatic potential V^H. Another advantage of the formulation in terms of analytic integrals is that the energy enjoys the full point group symmetry of the cluster which is not necessarily the case if the matrix elements were evaluated by a numerical integration over a cartesian mesh.

The above formulation allows the forces to be calculated semi-analytically using the Hellmann–Feynman theorem and numerical estimates of all the derivatives. It is important, however, to include the derivatives of the basis functions.

We have used basis sets of s and p gaussian orbitals although code has recently been written which extends these to any polynomial multiplied by a gaussian function. The second derivatives of the energy can also be calculated and used to obtain the vibrational modes of defects (Jones *et al.* 1991).

3. The strengths and weaknesses of the cluster method

For solid state problems there are a number of cases where cluster theory gives useful information but, in others, it is seriously unreliable.

For molecular solids, i.e. those composed of largely non-polar molecules like zero-dimensional phosphorous–selenide glasses (Jones & Lister 1989) or the fullerenes (Jones *et al.* 1992), the method is ideal as it can concentrate on the properties of the isolated molecules. This could also be true for polymers or liquid crystals. For covalently bonded solids or defects within them, it appears that H-termination is an extremely effective means of passivating the surface. The result is that structural and the higher phonon branches are well described. The lower modes and the elastic constants require longer ranged interactions (Kunc 1985) and so are more difficult to describe with the theory. The cohesive energy of the solid is also much more difficult to obtain because the basis can often be incomplete and because of the presence of the H atoms. The electronic gaps are, as stated above, much larger than they should be as it is well known that LDF theory leads to gaps smaller than those observed.

For point defects such as impurities or impurity aggregates, the method successfully gives structures in agreement with other LDF calculations (Jones 1989) but in addition the local modes of vibration of light impurities are reasonably well described. The migration or reorientation energy within the cluster can also be found such as for O in Si (Jones *et al.* 1991). The relative energies of H in various positions of the Si lattice agree well with other LDF calculations (Briddon & Jones 1990) but bond energies are usually too large. Recent work has focused on dislocations and their interaction with impurities (Heggie *et al.* 1992).

Graphite, a layered material, can also be treated with H atoms terminating layers of carbon atoms. Both interplanar and intraplanar lengths are determined to within a few percent of the observed values (C. D. Latham, personal communication).

Table 1. *Frequencies (in* cm^{-1}) *of local modes of* C$_i$–O$_i$

$^{12}C^{16}O^{28}Si$	$^{12}C^{18}O^{28}Si$	$^{13}C^{16}O^{28}Si$	$^{14}C^{16}O^{28}Si$	$^{12}C^{16}O^{30}Si$
calculated				
1141	1140	1101	1067	1136
925	925	898	874	917
625	624	624	624	604
604	598	604	604	589
565	562	564	564	550
559	558	558	558	541
observed				
1115.5	1115.5	1078.3	1047	
865.2	865.2	841.8	819.2	
742				
586 (72.6 meV)	582	586	586	576
550				
528 (65.5 meV)	523	528	528	

For H-bonded systems like ice, recent work (Heggie *et al.* 1992) indicates that the O–H distance between atoms belonging to different water molecules decreases with the cluster size as expected. This is an exciting discovery since it shows that the method may be applicable to biochemically important materials.

For silicates like quartz, the method gives excellent Si–O lengths and Si–O–Si, O–Si–O angles and the energy derivatives of distorted clusters can be used to fit classical potentials such as those of the Catlow–Sanders form. Thus has given very encouraging results for the properties of quartz under pressure (J. Purton, R. Jones, C. R. A. Catlow & M. Leslie, unpublished results). Ionic solids are best treated with a termination consisting of charge distributed around sites outside the cluster. For NaCl, MgO and Al_2O_3 the bond lengths are given to within few percent.

Thus there are a wide range of materials and their properties that can be explored using the cluster method.

The computationally most intensive routines are those involved in evaluating the three centred integrals but it is these which are most easy to vectorize and parallelize. Consequently, it is possible to relax an inner set of say 17 atoms of a 70 atom cluster in about three CPU days on an IBM RS6000 work station and evaluate the necessary second derivatives in about the same amount of time. This represents nowadays a modest computational requirement.

The ability to compute the forces on the atoms near the defect and to move them until equilibrium prevails has given in several cases quite unexpected results. It is these cases that are of the greatest interest for they show that our intuition has led us astray and this might then suggest a resolution of some long standing problem. I next describe an example of this sort which has given quite unexpected results.

4. Application to the interstitial carbon–oxygen defect in silicon

This is a complicated but important defect as it is one of the dominant defects produced in electron irradiated Si which contains C and O impurities. The defect is known to contain one O and C atom and its vibrational modes (Davies *et al.* 1986) are given in table 1. What is surprising is that the highest mode at 1115 cm^{-1} is unaffected by ^{18}O doping quite unlike bond centred interstitial oxygen (Newman 1973).

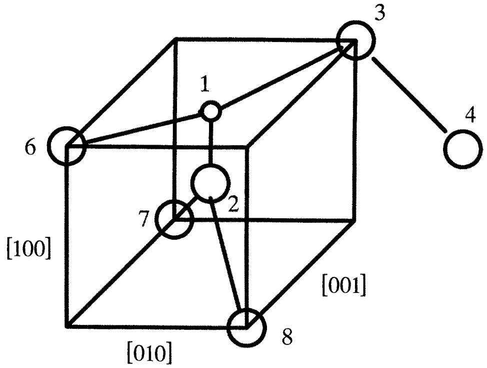

Figure 1. Schematic arrangement of atoms in the C_i split-interstitial. The small circle denotes a C atom. Note the dangling bonds on C and the central Si atom.

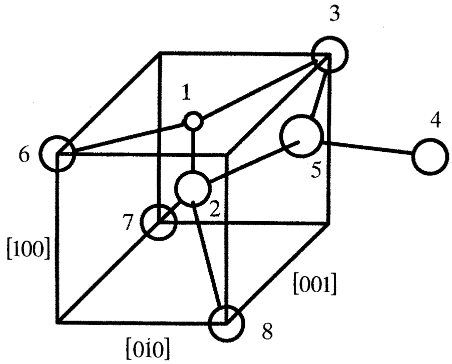

Figure 2. Schematic arrangement of atoms in C_i–O_i complex. The small circle represents the C atom and the large one the over-coordinated O atom.

Magnetic resonance experiments (Trombetta & Watkins 1987) showed that the structure of the defect must be closely related to that of the C split-interstitial (Watkins & Brower 1976) illustrated in figure 1, and they suggested that the C atom has a filled dangling bond parallel to, say [01$\bar{1}$], and is bonded to a Si atom with an empty dangling bond nearly parallel to [011], with O occupying a bond centred location between atoms 3 and 4 of figure 1. Now this model would assign the 1115 cm^{-1} mode to an O stretch mode which is inconsistent with the insensitivity of this mode to ^{18}O substitution.

The LDF cluster calculations (Jones & Öberg 1992) revealed very unusual bonding in the defect. The C, O and 17 Si atoms of a 73 atom H-terminated cluster $COSi_{35}H_{36}$ centred on the Trombetta–Watkins model of the defect were relaxed. We found that the O-atom moved away from the bond centred position towards the middle of the quadrilateral (in the (01$\bar{1}$) plane) formed by atoms 1, 2, 3 and 4 in figure 2. The reason is that the Si dangling bond has an empty level lying above that of C. It can lower the energy of one set of lone pair electrons on O (atom 5) by forming a dative bond and pulling O towards it. Consequently O becomes over-coordinated. This model explains why O prefers to bind to the defect in the same plane as the Si dangling bond.

The vibrational modes of O are expected to be low lying because of the very long

Si–O lengths (*ca.* 0.185 nm) present in the over-coordinated O defect. The energy second derivatives between the atoms 1 to 8 in figure 2 were calculated and inserted into the dynamical matrix. The calculated frequencies of the six highest modes of C_i–O_i and their isotopic shifts are given in table 1.

The absolute values of the frequencies are within about 100 cm^{-1} of the observed ones but their isotopic shifts are given very well. This strongly suggests that the structure found here is the correct one.

To conclude, the calculations showed that interstitial O is unstable when close to a Si dangling bond and readily forms an over-coordinated defect with rather long Si–O bonds and low lying Si–O stretch modes. This is of interest to the more complex problem of O precipitation where Si interstitials might rise from the precipitation process and interact with other O complexes. Presumably some weak or broken bonds will be formed in these processes. These may well be attacked by O and form over-coordinated defects with low lying vibrational modes. I point out that no high frequency O related modes have been found for the thermal donor and it is tempting to speculate that this may be because the O atoms in that case are also over coordinated. There have been models of thermal donors along these lines (Chadi 1990; Jones 1990; Deak *et al.* 1991).

5. Conclusions

I have shown in this paper that the cluster LDF method can reveal the structure and electronic properties of a wide range of solids and especially their defects. The calculations have in several cases given surprising and unexpected results which may – and often does – explain some interesting phenomena. I believe that the method can be profitably used for a variety of defects and defect processes in many materials and enjoys a considerable advantage, for a first-principles one, in that it requires only a moderately significant computational effort.

It is a pleasure to acknowledge helpful discussions with a large number of colleagues. Special thanks are owed to P. R. Briddon, M. I. Heggie, G. M. S. Lister, C. D. Latham, S. Maynard, R. C. Newman, S. Öberg, M. Stoneham, V. Torres and A. Umerski.

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Discussion

P. C. H. Mitchell (*Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.*): An impressive feature of your *ab initio* calculations is that they reveal the probable presence of three-coordinate oxygen at a defect site. There are a number of classic neutral molecular complexes having over-coordinate oxygen, e.g. basic beryllium and basic zinc acetate; $M_4O(O_2C.CH_3)_6$, (M = Be,Zn). In these structures a four-coordinate oxygen atom, at the centre of a tetrahedron of four metal atoms, forms a bond to each metal atom. The two oxygen atoms of each acetate bind to two different zinc atoms; the acetates thereby act as bridging groups along each edge of the tetrahedron of metal atoms. These structures would seem to offer an excellent means of testing out the computational procedure with well-characterized neutral molecules.

R. Jones: This suggestion is a good one and one I would like to follow-up.