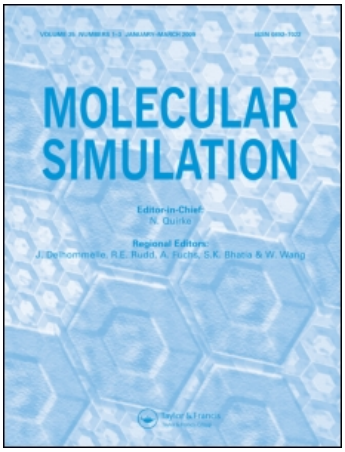

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The Practical Calculation of Interionic Potentials in Solids using Electron Gas Theory

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THE PRACTICAL CALCULATION OF INTERIONIC POTENTIALS IN SOLIDS USING ELECTRON GAS THEORY

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A review is presented of the ways in which electron gas theory has been used to obtain interionic potentials in solids. The strengths and limitations of such non-empirical potentials, and of the methods used to generate them, are emphasized. After minor modifications, many of the functionals derived from electron gas theory turn out to be much more successful and much more widely applicable than might have been expected, given their underlying assumptions.

KEY WORDS: Electron gas theory, interionic potentials

INTRODUCTION

The atomistic simulation of increasingly complex materials, often of considerable technological and industrial importance, demands reliable potentials that can be evaluated quickly and cheaply. Modelling the bulk and surface properties of such materials, as well as lattice, substitutional and electronic defects, on which many of the chemical and physical properties depend, places strict requirements not only on the accuracy of the potentials but also on their derivatives.

The first step in modelling ionic solids is usually to assign integral charges to the constituent ions. This procedure does not contain any implicit assumptions that the bonding in the material is purely ionic: for our present purposes, the suitability of the model is judged solely by its ability to reproduce or predict accurately the properties of interest. Of course, the assignment of charges for materials which are believed to be highly ionic is very straightforward.

The next step is to provide an adequate description of the short-range interactions between the electron clouds of the ions, and this can be a formidable task. In this article we consider only the use of two-body potentials to specify these interactions and we discuss one of the simplest methods that has been used for the direct calculation of such potentials from first principles. We use the label 'non-Coulombic' for that part of the total energy which does not arise from the Coulombic interactions between the formal charges of the ions.

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One alternative is to use empirical potentials fitted to experimental data. Historically, the most common approach [1] has been to use simple Born-Mayer, Buckingham or Morse functions with parameters optimized so as to reproduce various properties of the perfect lattice, such as lattice constants, lattice energy, elastic constants or phonon dispersion curves.

For a material with n different ionic species, there are $\frac{1}{2}$ n(n + 1) distinct potentials, each with its own set of parameters to be fitted. Of course, properties of the perfect lattice can only yield information for ions close to their equilibrium separation. In materials with high symmetry this means that the potentials are sampled only at a very small number of interionic separations. In order to study surface structures and properties of defective lattices it is essential to take explicit account of relaxation effects, so that it is vital to describe the interactions at internuclear separations far from equilibrium. The same is true for predicting the properties of perfect lattices at high pressure. Thus, even if there are sufficient experimental data to fit all of the free parameters, the severe approximations made in choosing the functional forms of the empirical potentials can still lead to poor results. For example, it seems unlikely that a single exponential term could account for the non-Coulombic repulsion over a very wide range of internuclear separation. The treatment of electronic defects presents a further set of problems: we cannot determine in any consistent fashion the potentials involving ions which carry formal changes different from those in the perfect crystal. This is especially true for anions, where the spatial extent of the electron cloud varies considerably with the net charge. In turn, this means that it is difficult with empirical potentials to consider many important processes such as oxidation and reduction.

The reasons for preferring calculations of non-empirical interionic potentials in solids are thus very clear. Electron gas theory, which is one of the simplest formulations of density functional theory, has been used very widely for this purpose, and it is the subject of this article. In that we are concerned here with interactions between ions, some of our later remarks will not necessarily be valid for the non-ionic systems to which the electron gas models have also been applied.

The structure of this review is as follows. We start with an outline of electron gas theory as applied to the calculation of interionic potentials. There have been many variants of this general approach; this account is not intended to be an exhaustive survey, but the interested reader is referred to the literature cited (in particular see the comprehensive review of Clugston [2]). We then examine the assumptions made in the electron gas approach and, based on a study of some small diatomic molecules for which accurate wavefunctions are available, possible alternative formulations are suggested. Of course, even if some of the approximations used in the calculation of the potentials are crude, so that there are some lattice properties which are not reproduced to the desired accuracy, such calculations are still invaluable for indicating the functional form that the potential must take. Finally, we make some general remarks concerning the practical use of electron gas potentials and their transferability from one crystal environment to another.

THEORY

Although density functional methodology is widely used to calculate interionic potentials, this does not usually involve a direct variational calculation of the interaction energy. There have been some attempts to obtain inert-gas potentials by direct solution of the Thomas–Fermi–Dirac equations [3–6], but to our knowledge no one

has treated ion–ion interactions in this manner. The procedure now most commonly used is based on the suggestions of many workers [7–14] and developed considerably by Gordon and co-workers [15–27]. This approach is usually associated with the names of Kim and Gordon [15].

In this model, Hartree-Fock electron densities for the isolated species, ρ_A and ρ_B, are used to evaluate the electron density in the interacting system ρ_{AB}. The densities are assumed to be additive:

$$\rho_{AB}(r) = \rho_A(r) + \rho_B(r) \tag{1}$$

This is likely to be an excellent approximation for the interactions of ions. For more covalent interactions, there will be some distortion of the individual electron distributions and also some rearrangement of the electron density into the region betweeen A and B.

The next step involves relating the energies of A, B and AB directly to the corresponding electron densities. It is, of course, more usual in quantum mechanics to work with the wavefunctions, but Hohenberg and Kohn [28] have shown that the ground state energy E of any system is a functional of the electron density ρ. The exact form of the relationship between E and ρ is not known.

Using the additive approximation (1), the interaction energy E_{int} for A and B separated by R can be written

$$\begin{aligned} E_{int}(R) &= E_{AB}(R) - E_A - E_B \\ &= E[\rho_{AB}] - E[\rho] - E[\rho_B] \\ &= E[\rho_A + \rho_B] - E[\rho_A] - E[\rho_B] \end{aligned} \tag{2}$$

The next step is the evaluation of $E[\rho]$. We start by considering the Hartree-Fock energy E_{HF}, which can be partitioned according to

$$E_{HF} = E_T + E_{coul} + E_{ex} \tag{3}$$

where E_T is the kinetic energy, E_{coul} arises from all the Coulombic interactions involving nuclear charges and electron charge clouds, and E_{ex} is the exchange energy. Given the Hartree-Fock electron density, we can evaluate E_{coul} exactly. The same is not true for E_T and E_{ex}. The difference between E_{HF} and the exact non-relativistic energy E is usually called the correlation energy, E_{corr}.

In the approach described in this review, approximations to each of E_T, E_{ex} and E_{corr} are evaluated from the Hartree-Fock electron density ρ using functionals suggested by electron gas theory, which is the simplest form of density functional theory. Thus,

$$E = E_T[\rho] + E_{coul} + E_{ex}[\rho] + E_{corr}[\rho] \tag{4}$$

The functionals used are derived for a uniform (homogenous) electron gas [29], which is not a good approximation near the nuclei [30]. However, the contributions from these nuclear regions to the total energy of the interacting system will be essentially the same as the sum of the corresponding contributions in the separate ions, so that the effects of the nuclear regions can be assumed to cancel from E_{int}. There are other possibilities for cancellation of errors in each of the components of the energy.

The functionals most commonly used for E_T and E_{ex} take the form

$$\begin{aligned} E_T[\rho] &= c_k \int \rho(r)^{5/3} dr \\ &\equiv c_k I_2 \end{aligned} \tag{5}$$

with

$$\begin{aligned} c_k &= (3/10)(3\pi^2)^{2/3}, \text{ and} \\ E_{ex}[\rho] &= c_e \int \rho(r)^{4/3} dr \\ &\equiv c_e I_1 \end{aligned} \tag{6}$$

with $c_e = -(3/4)(3/\pi)^{1/3}$. It is important to note that E_{ex}, the Dirac-Slater exchange energy, includes self-interaction terms. For example, it is clear from the form of (6) that $E_{ex}[\rho]$ is non-zero for a one-electron system as the hydrogen atom.

For E_{corr}, it is common to use

$$E_{corr}[\rho] = \int \varepsilon_{corr}\, \rho(r) dr \tag{7}$$

where

$$\varepsilon_{corr} = \begin{cases} +0.0311\ \ln(r_s) - 0.048 + 0.009\, r_s \ln(r_s) - 0.01\, r_s & r_s \leqslant 0.7 \\ -0.06156 + 0.01898\ \ln(r_s) & 0.7 < r_s < 10 \\ -0.438\, r_s^{-1} + 1.325\, r_s^{-3/2} - 1.47\, r_s^{-2} - 0.4\, r_s^{-5/2} & r_s \geqslant 10 \end{cases} \tag{8}$$

with $r_s^3 = 3/(4\pi\rho(r))$ [31,32].

Using these functionals, we can now evaluate the interaction energy directly from the Hartree-Fock electron densities of A and B. Gordon and Kim [15] have shown how to manipulate the right-hand side of (2) so as to minimize numerical errors in E_{int}, which is typically three orders of magnitude smaller than $E[\rho_A + \rho_B]$. There are three additional points to be stressed.

The first of these relates to the self-interaction contributions incorporated in $E_{ex}[\rho]$. These lead to spurious long-range minima in E_{int} [15] and, if next-nearest-neighbour interactions are included in the non-Coulombic contributions for solids, lattice energies are typically overestimated by 10% [33]. A correction due to Rae [34] is frequently used according to which exchange energy is scaled:

$$E_{ex}[\rho] \rightarrow \gamma(N)\, E_{ex}[\rho] \tag{9}$$

where

$$\gamma(N) = (3 - 8\delta + 6\delta^2 - \delta^4)/3 \tag{10}$$

and δ is defined in terms of the total number of electrons N by

$$(N)^{-1} = \frac{1}{2}(8\delta^3 - 9\delta^4 + 2) \tag{11}$$

We shall return later to this question.

The second point is that we must take at least some account of the crystal environment when selecting the Hartree-Fock electron densities to be used in the various functionals. For example, O^{2-} is unstable in the gas phase but occurs widely in crystalline solids. The usual approach for anions [33] is to solve the Hartree-Fock equations in an external spherical potential chosen to reproduce the Madelung

potential at the relevant crystal site. For cations, the free ion densities have been found to be sufficient.

Finally, the functionals in equations (5–8) have been derived for closed-shell systems. It is also possible to derive functionals for the case in which no electrons are paired. For most open-shell systems, which lie between these two limits, we could choose to use spin density functional theory [35] which provides functionals that depend explicitly on the degree of spin polarization. However, the dependence of the Hartree-Fock density on the electron configuration means that the effects of electron spin have already been taken into account to a large extent. Thus it is not clear in the present context which functionals should be used. For solids such as transition metal oxides the "closed-shell' functionals have proved to be satisfactory.

POTENTIALS

It is not appropriate to refer in detail to the very large body of work that has now been carried out using 'non-empirical' potentials obtained from electron gas theory. The range of materials considered has expanded considerably from early work on highly symmetric binary compounds to present work on ternary and quaternary oxide [36] and halide systems [37]. Early work on perfect lattice properties was carried out by Kim and Gordon [19], by Cohen and Gordon [20,21], and by Wedepohl [38,39]. Early applications to defect calculations include the work of Keeton and Wilson [40], of Dienes *et al.* [41], and of Catlow and co-workers [42,43].

It is important to note that the majority of calculations have used the shell model [44] to allow for the effects of ionic polarization. In this model the interionic potentials act between the massless shells of the ions. The shell parameters, i.e. the shell charges and the spring constants of the harmonic springs coupling cores and shells, are determined empirically, generally by fitting to dielectric or phonon data. The shell model can be thought of as an additional term in each of the interionic potentials [45], so that some additional empiricism has been introduced.

For work on fluorides the reader is referred to Ref. 46, and for oxides to References 47 and 48. Very briefly, for oxides with potentials generated as above using the Rae correction [34], lattice constants tend to be slightly overestimated: errors typically $< 1\%$ for ionic oxides (such as MgO, CaO, SrO, BaO) with larger errors, $\approx 2\%$, for oxides with more 'covalent' character (MnO, CdO, PbO_2, UO_2).

It is very encouraging that potentials obtained in different ways generally lead to similar conclusions about many perfect and defective lattice properties. Nevertheless this is not always the case, particularly when the interionic distances involved may be far from those in the perfect lattice in equilibrium. Figure 1 shows the non-Coulombic contributions to the interionic potentials for O^{2-}–O^{2-} in MgO obtained empirically [49], from electron gas theory [33] and from *ab initio* procedures [50]. At the perfect lattice separations (3.0 Å for O^{2-}–O^{2-}) there are only small differences between these potentials, and so the calculated bulk lattice properties are generally similar. The situation for very much shorter internuclear separations is very different. The empirical $O^{2-} - O^{2-}$ potential is attractive for all interionic separations whereas the electron gas and *ab initio* potentials are repulsive. The O^{2-}–O^{2-} distance relevant to anion interstitial formation is < 2 Å and there is a difference of over 5 eV in the anion interstitial energy [1]. Calculated migration energies of O^{2-} are also different [1].

A similar situation applies for Al_2O_3 where very different defect structures are

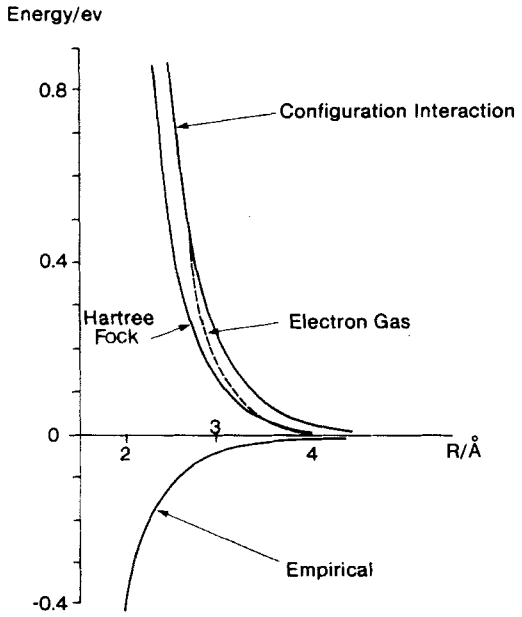

Figure 1 A comparison of non-Coulombic potentials in MgO for O^{2-}–O^{2-}. The empirical potential is taken from [49], the electron gas potential from [33], and the *ab initio* potentials from [50].

predicted from empirical and electron gas potentials, again largely due to the different $O^{2-} - O^{2-}$ potentials. An empirical potential [51] predicts that (per defect) the Schottky defect energy is larger than the anion Frenkel energy; the reverse is true for electron gas potentials [41,51].

A further example of different predictions from empirical [51] and electron gas potentials [41,51], which in principle could be resolved experimentally, concerns the surface structure of α-Al_2O_3. Empirical potentials lead to the following order of stability for the five lowest-index surfaces:

$$\text{unrelaxed: } \{10\bar{1}2\} < \{11\bar{2}0\} < \{10\bar{1}1\} < \{0001\} < \{10\bar{1}0\}$$

$$\text{relaxed: } \{10\bar{1}2\} < \{11\bar{2}0\} < \{10\bar{1}0\} < \{0001\} < \{10\bar{1}1\}$$

to be compared with

$$\text{unrelaxed: } \{10\bar{1}2\} < \{11\bar{2}0\} < \{10\bar{1}1\} < \{0001\} < \{10\bar{1}0\}$$

$$\text{relaxed: } \{0001\} < \{10\bar{1}0\} < \{10\bar{1}2\} < \{11\bar{2}0\} \approx \{10\bar{1}1\}$$

from electron gas potentials. For unrelaxed surfaces, with atoms at the same positions as in the bulk lattice, the two potentials predict identical orders. The differences between the two potentials at shorter distances, sampled when the surfaces relax inwards towards their equilibrium positions, lead to different surface structures and energies. Differences of up to 50% occur for individual surface energies (see Table 1), and these lead in turn to different crystal morphologies as shown in Figure 2.

For oxides it is also important to note the extensive use of atomistic simulation techniques to consider electronic defects and hence their redox properties [47]. It is straightforward to obtain an appropriate Hartree-Fock electron density for O^-,

Table 1 Surface energies (in J/m^2) for α-Al_2O_3 calculated using electron gas and empirical potentials.

Surface	*Empirical*		*Electron gas*	
	unrelaxed	*relaxed*	*unrelaxed*	*relaxed*
{0001}	6.53	2.97	5.95	2.03
{10$\bar{1}$0}	6.87	2.89	6.46	2.23
{10$\bar{1}$2}	3.55	2.57	3.63	2.29
{11$\bar{2}$0}	5.17	2.65	4.37	2.50
{10$\bar{1}$1}	6.41	3.27	5.58	2.52

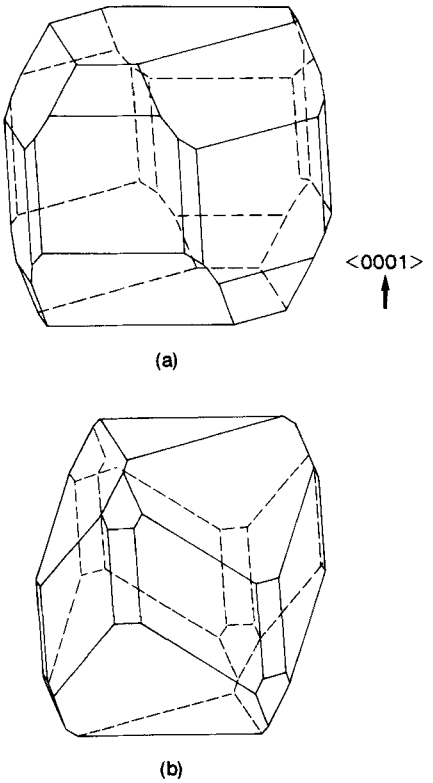

Figure 2 Calculated morphologies of α-Al_2O_3 based on (a) electron gas and (b) empirical potentials.

rather than O^{2-}, and hence in a consistent fashion to derive a complete set of potentials for this species.

We now turn to consider in more detail the approximations used in the electron gas method.

ELECTRON GAS APPROXIMATIONS

The electron gas model outlined in a previous Section implies that kinetic, exchange and correlation energies are given by appropriate functionals of the electron density.

There is no reason *a priori* why the substitution of Hartree-Fock densities into free electron gas functionals should produce the corresponding Hartree-Fock energies. However, within the spirit of the Kim-Gordon approach, such a result would be reassuring while also indicating possible future developments of the model.

Allan *et al.* [52] have used SCF wavefunctions, calculated with a large flexible basis set (a universal even-tempered basis set of 9s/6p/3d Slater-type functions on each centre), to test expressions such as (5) and (6). For the series of light diatomic molecules and singly-charged positive ions considered, it can be seen from Table 2 and Figure 3(a) that a linear relationship between the Hartree-Fock kinetic energy and I_2 (equation (5)) is obeyed rather well. The gradient of the least-squares fitted line is 3.15 and the intercept is 0.34. The gradient of the least-squares fitted line constrained to pass through the origin is 3.16; this proportionality constant is larger than the value of c_k predicted for the free electron gas (equation (5)) by $\approx 10\%$. The errors are no larger for open-shell systems provided that open-shell restricted Hartree-Fock densities are substituted directly into (5). Equation (5) seems to be more widely applicable than its derivation might suggest.

Table 2 Values of the integral I_2 (equation (5)), the kinetic energy (K.E.), the integral I_1 (equation (6)), the Dirac-Slater exchange energy E_K (equation (12)), and the self-interaction term for a series of light atoms and molecules. Each system is in its ground electronic state, and the bond lengths for the molecules are close to their equilibrium values. All the quantities are listed in atomic units.

System	I_2	*K.E.*	I_1	E_K	*'Self-interaction'*
Be	4.573	14.573	3.131	2.667	2.616
BeH^+	4.735	15.040	3.420	2.916	2.870
BeH	4.746	15.151			
BH^+	7.741	24.784			
BH	7.881	25.120	4.898	4.129	3.912
CH	11.962	38.254	6.446	5.411	4.939
NH	17.186	54.916	8.280	6.911	6.100
OH	23.727	75.380	10.410	8.555	7.391
LiO	25.917	82.294			
HF	31.731	99.921	12.817	10.399	8.781
N_2	34.267	108.61	15.983	13.061	7.626
CO	35.619	112.66	16.307	13.334	11.715
Ne	41.019	128.55	14.939	12.108	10.104
O_2	47.084	149.29	19.973	16.248	8.925
F_2	62.879	198.51	24.613	19.931	10.211

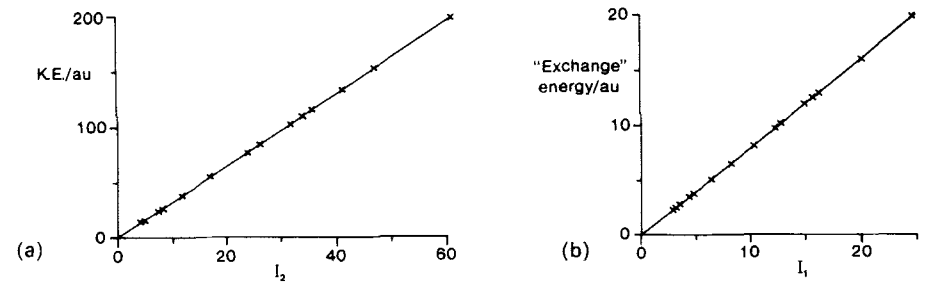

Figure 3 Test of equations (5) and (6) for a series of light molecules. (a) Hartree-Fock kinetic energy (K.E.) versus I_2. (b) Exchange energy E_K (equation (12)) versus I_1.

The Dirac-Slater exchange energy $E_{ex}[\rho]$ can be linked to appropriate Hartree-Fock energies $-E_K$ for both open- and closed-shell molecules [53]:

$$E_K = \sum_{i<j}{}' K_{ij} + \tfrac{1}{2}\sum_i J_{ii} \tag{12}$$

where N is the number of electrons, J_{ij} and K_{ij} are Coulomb and exchange integrals (in which i and J label spin-orbitals), and the prime indicates that the first summation is only over pairs of the same spin. The 'usual' definition of exchange energy consists of just the first term - the second term in (12) is the 'self-interaction' energy referred to earlier. This self-interaction energy has a contribution from each electron and can dominate for small numbers of electrons (see Table 2). As can be seen from Figure 3(b), the linear relationship between E_K and I_1 suggested by (6) is also obeyed reasonably well. The gradient of the least-squares line is 0.803 and the intercept is 0.19. The gradient of the least-squares fitted line constrained to pass through the origin is 0.815; as was the case for the kinetic energy term, this proportionality constant is not that predicted by (6). Equation (6) underestimates $|c_e|$ by $\approx 10\%$. Again errors are no larger for the open-shell molecules - in the present context it does not appear to be necessary to distinguish between closed- and open-shell systems.

There are problems with the simplest version of the Rae correction (equations (9–11)). In that $E_{ex}[\rho]$ is scaled by a parameter δ which depends only on the total number of electrons N, it is not clear how the correction should be applied in the polyatomic case. For example, Table 2 shows that the E_K values are fairly similar in the isoelectronic molecules CO and N_2 (13.33 and 13.06 hartree) whereas the self-interaction terms are very different (11.71 and 7.63 hartree).

In Rae's original work [34], N was taken to be the total number of electrons not only for the case of the interacting systems but also for each of the separated atoms. This is the most common procedure for interionic potentials. Subsequently, Lloyd and Pugh [54] suggested that this number should be put equal to the total number of valence electrons in the two atoms. Waldmann and Gordon [25] have also considered this problem and used a scaling factor, derived from studies of the atomic self-exchange terms, which is a function of the total number of valence electrons. These schemes still suffer from the problem that isoelectronic systems, or indeed isovalent systems, have the same scaling of the exchange energy. Rae [55] has suggested a linear extrapolation on $\gamma(N)$ such that

$$\gamma(N) = (\rho_A\gamma(N_A) + \rho_B\gamma(N_B))/(\rho_A + \rho_B) \tag{13}$$

where N_A and N_B are the numbers of valence electrons on the two atoms. Note that $\gamma(N)$ now depends on the electron densities so that the exchange energy contribution to the interaction energy is given by

$$\int\{\gamma(N_A)\rho_A[(\rho_A + \rho_B)^{1/3} - \rho_A^{1/3}] + \gamma(N_B)\rho_B[(\rho_A + \rho_B)^{1/3} - \rho_B^{1/3}]\}\,d\mathbf{r} \tag{14}$$

Of course, for very large numbers of electrons, the self-exchange contribution can be considered negligible (as a proportion of the total energy).

To apply the functionals to the calculation of interaction energies it is also important to examine whether the functionals are obeyed for single systems over wide ranges of internuclear separation. This is, of course, a much finer test of such functionals. Allan and Cooper [53,56] have considered several light diatomic molecules, including LiH^+, LiH, BeH, BH^+ and OH, using correlated wavefunctions which allow for correct dissociation. We describe here the results for the BH^+ and

LiH^+ ions, which have very different bonding characteristics. These ions were described using spin-coupled wavefunctions [57,58], which provide accurate potential curves and properties, as well as highly visual representations of the bonding.

Plots of the kinetic energy versus I_2 for the $X^2\Sigma^+$ states of BH^+ and LiH^+ are shown in Figures 4(a) and (b). BH^+ is bound by more than 180 kJ mol^{-1} and, as discussed in detail in Reference 59, there is a rapid change in the mode of spin coupling between nuclear separations of 3 and 4 bohr from an atomic situation (B^+ and H) to values characteristic of the new single bond. Molecule formation is also clearly visible in position space and momentum space electron density plots [60]. Figure 4(a) shows that even for a covalently bonded system the proportionality between the kinetic energy and I_2 (equation 5) holds over restricted ranges of internuclear separation R. At short R the proportionality holds for about 1 bohr around $R_e \approx 2.5$ bohr. The plot has a pronounced minimum near $R_e \approx 3.3$ bohr. Figure 3(a) therefore suggests a dramatic change between two different electron configurations, assuming that the gradients of the plots before and after the minimum are a reflection of this electronic configuration. This is, of course, consistent with the variation of the spin-coupling coefficients.

The $X^2\Sigma^+$ state of LiH^+, on the other hand, is only very weakly bound ($D_e \approx 12$ kJ mol^{-1}, $R_e \approx 4.2$ bohr). Neither the mode of spin coupling nor the spatial wavefunction changes significantly with R. The small binding energy in this case arises largely from induction with only a small contribution from dispersion. The linear relationship between the kinetic energy and I_2 is obeyed for all R (Figure 4(b)). Provided that the success for LiH^+ of functionals such as (5) is general for other systems with no significant change in bonding character with R, then this is very encouraging. The results for molecules such as BH^+ suggest that even for covalently bonded systems, the functionals are useful over wide ranges of internuclear separation.

Several modifications have been suggested for the correlation energy term [18,26,34,61–66]. There are problems in attempting to treat an essentially non-local term with a local functional that depends only on the electron density. The correlation energy functional equation (8) is known to overestimate the correlation energy of atoms by a factor of two [16].

Some authors have added dispersion terms to a correlation energy functional [34,55,63,64,65] - others have replaced it entirely at large R with such dispersion terms

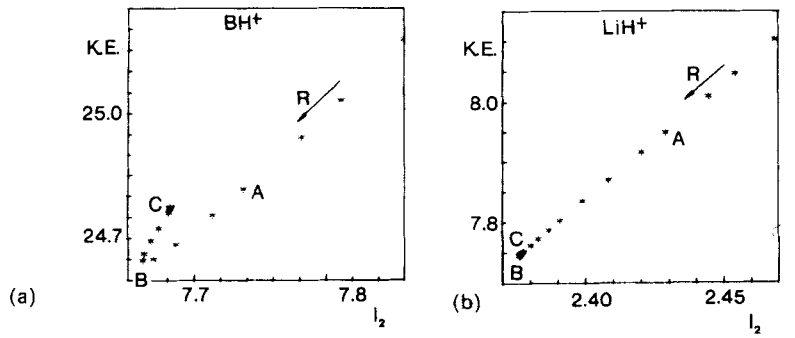

Figure 4 Kinetic energy (K.E.) versus I_2 for the spin-coupled descriptions of the $X^2\Sigma^+$ ground states of BH^+ ($R_e \approx 2.3$ bohr) and LiH^+ ($R_e \approx 4.2$ bohr). (a) BH^+ - the points marked are A = 2.3501 bohr, B = 3.3 bohr, and C = 6.0 bohr. (b) LiH^+ - the points marked are A = 2.3501 bohr, B = 5.5 bohr, and C = 8.0 bohr.

[61]. It is not clear that dispersion energies can be estimated from local density functionals. In addition, coefficients of R^{-6} terms derived from Hartree-Fock densities cannot refer to dispersion, since electron correlation is excluded. Empirical approaches based on calculations with highly correlated wavefunctions should be more useful here [56].

Waldman and Gordon [25] replaced the functionals in equations (5–8) for the kinetic, exchange and correlation energies. Based on studies of atoms [16], they modified the values of c_k and c_e. In addition, instead of using a correlation energy functional, they employed a Drude (oscillator) model [26,66,67], similar in spirit to the shell model. They did not study ion-ion interactions using these variations of the model. However, Cohen and Gordon [20,21] had previously studied perfect lattice properties of oxides and halides using modified values of c_k and c_e, although still using a scaled correlation energy rather than a Drude model.

In the same spirit, Allan and Cooper [56] scaled the functionals for the kinetic and exchange energies using values for c_k and c_e suggested from their molecular studies. Their new value of c_k is very similar to that of Waldmann and Gordon [25], but the values of $|c_e|$ are very different. Allan and Cooper [56] increased $|c_e|$ by $\approx 10\%$ from that given by (6), whereas Waldman and Gordon [25] reduced $|c_e|$ from the free electron gas value, in an attempt to allow for self-interaction contributions. For the reasons outlined previously, Allan and Cooper [56] did not correct for the self-interaction energy, relying instead on the partial cancellation of the contributions in the interacting and isolated systems. Based on a suggestion of Robles and Kemister [68], and also a study of appropriately defined 'correlation energies' for LiH and BeH over a wide range of nuclear separation [56], they took the correlation energy to be proportional to the exchange energy and hence to I_1. Potentials for MgO, MgF_2 and Na_2O were obtained using these functionals and, within the shell model, perfect and defective lattice properties were predicted to an accuracy comparable to that achieved using potentials obtained within the more usual formulation outlined earlier in this paper.

It is, of course, a difficult problem to find suitable and consistent values for the scaling parameters used in such a modified approach. This is particularly true for systems consisting of both light and heavy atoms, for which an interpolation similar to that in (14) might be successful. For light systems c_k and c_e should be modified from the free electron gas values. However, in the limit of infinite nuclear charge, (5) and (6) become the exact non-relativistic functionals [69], and so they are likely to be more accurate for heavier systems.

An alternative approach, which has been very little explored, is the use of gradient terms in the functionals to allow for the inhomogeneity of the electron density. For example, we can expand the kinetic energy $T = E_T(\rho)$ according to

$$T = T_0 + T_2 + T_4 + \ldots \tag{15}$$

where

$$T_0 = (3/10)(3\pi^2)^{2/3}\int \rho^{5/3} \mathrm{d}r \tag{16}$$

$$T_2 = \frac{1}{72}\int \frac{(\nabla\rho)^2}{\rho}\,\mathrm{d}r \tag{17}$$

$$T_4 = \frac{1}{540(3\pi^2)^{2/3}}\int \rho^{1/3}\left\{\left(\frac{\nabla^2\rho}{\rho}\right)^2 - (9/8)\left(\frac{\nabla^2\rho}{\rho}\right)\left(\frac{\nabla\rho}{\rho}\right)^2\right.$$

$$+ (1/3)\left(\frac{\nabla\rho}{\rho}\right)^4\Big\}dr \qquad (18)$$

Note that equation (16) is equivalent to (5).

There are several problems with this gradient expansion. Shih [70] showed that incorporation of T_2 directly into (4) leads to much poorer inert gas - inert gas potentials. In addition, T_6 diverges. However, Pearson and Gordon [27] have suggested a means for dealing with this divergence problem [71]. At each point in space the gradient corrections are considered as terms in an asymptotic series which is then truncated at the smallest term. Pearson and Gordon [27], who refer to their scheme as a local asymptotic summation, have also examined scaling this smallest gradient correction by a factor between zero and one. This approach gives good estimates (errors $< 0.3\%$) for the total kinetic energies of the series of light molecules considered earlier [53], and Pearson and Gordon [27] have obtained very good inert gas - inert gas potentials using this scheme. It has not, as yet, been applied to interionic potentials.

In this context it is worth mentioning the work of Chelikowsky [72]. He showed that atomic energy terms alone are sufficient to predict accurately the cohesive energies of simple metals. This work is based on Teller's theorem [73], which states that direct solution of density functional theory equations will always lead to unbound solutions for polynuclear systems if corrections for inhomogeneity are omitted from the functionals. This implies that if both the metal and the isolated atom were true free electron gas (Thomas-Fermi) systems then there would be no binding. In Chelikowsky's model it is the increased homogeneity of the kinetic energy of the valence electrons in the metal that leads to the binding.

DISCUSSION AND CONCLUSIONS

Potentials generated from the electron gas methods seem to be much more successful than would be expected from the approximations of the very simple model. Even the simplest free electron gas functionals are much more widely applicable than might be expected from the underlying assumptions in their derivations. In particular, errors appear to be no larger for open-shell systems. However the proportionality constants are not those predicted by free electron gas theory, and differ from molecule to molecule [53]. In the case of covalently bonded systems, c_k and c_e also vary with internuclear distance [53].

The electron gas method provides a very cheap and efficient way of calculating, from first principles, interionic potentials over wide ranges of ionic separations. The method can be applied to any ion, independent of atomic number. Explicit account of the crystal environment is incorporated to the extent that an anion electron density can be used that is appropriate to the compound of interest. Furthermore, this approach provides a consistent framework for the evaluation of potentials involving substitutional and electronic defects.

In practice, it does not appear necessary to evaluate, for example, a different anion-anion potential for each different compound. Non-empirical anion-anion potentials appear to be highly transferable for a wide range of oxides and fluorides. This is especially useful for studies of ternary and quaternary systems. In such studies, a set of potentials for a wide range of binary oxides [36] and fluorides [37] were

obtained, all of which used the same anion-anion potentials and the same set of anion shell parameters. These were then used for the more complex systems, without modification.

For compounds with more covalent character, non-empirical potentials have been very useful for indicating appropriate functional forms for empirical potentials [74,75].

On the computational side it is difficult to foresee directions for future work. There is still considerable scope for improved kinetic energy, exchange and correlation functionals, including the further successful incorporation of gradient terms. Such functionals are important in several other applications of density functional theory, such as the Car-Parinello method [76].

At the very least, for electron gas methods to be widely applicable to more covalent systems, a criterion more elaborate than equation (1) is required for superimposing the separate ion densities [77]. Inevitably, much of the computational simplicity will then have been lost. In addition, many-body effects will be important. Small but very important interactions, such as crystal field effects, Jahn-Teller distortions and magnetic effects, need to be incorporated in a consistent fashion - all of these will serve as very stringent tests of any new method of generating potentials. Ultimately it may prove to be more desirable to use higher accuracy 'first principles' approaches than to try continually to improve upon the electron gas methods.

References

[1] C.R.A. Catlow, M. Dixon and W.C. Mackrodt, "Interionic potentials in ionic solids", in *Computer Simulation of Solids*, C.R.A. Catlow and W.C. Mackrodt, eds, Springer-Verlag, Berlin, 1982, Ch. 10.

[2] M.J. Clugston, "The calculation of intermolecular forces. A critical examination of the Gordon-Kim model", *Adv. in Physics*, **27**, 893 (1978).

[3] J.W. Sheldon, "Use of the statistical field approximation in molecular physics", *Phys. Rev.*, **99**, 1291 (1955).

[4] J. Goodisman, *Diatomic Interaction Potential Theory*, Academic Press, New York, 1973, Vols. 1 & 2.

[5] Y. Yonei and J. Goodisman, "Accurate Thomas-Fermi-Dirac calculations for diatomic systems", *Int. J. Quant. Chem.*, **11**, 163 (1977).

[6] I.G. Kaplan, *Introduction to Theory of Intermolecular Interactions*, Nauka, Moscow, 1982 (in Russian). Translation: *Theory of Molecular Interactions*, Elsevier, Amsterdam, 1985.

[7] K. Fuchs, "A quatum mechanical investigation of the cohesive forces of metallic copper", *Proc. Roy. Soc. Lond. A*,**151**, 585 (1935).

[8] K. Fuchs, "A quantum mechanical calculation of the elastic constants of monovalent metals", *Proc. Roy. Soc. Lond. A*, **153**, 622 (1936).

[9] H. Jensen, "Über die Existenz negativer Ionen im Rahmen des statistischen Modells", *Z. Phys.*, **101**, 141 (1936).

[10] D.W. Sida, "The scattering of positive ions by neutral atoms", *Phil. Mag.*, **2**, 761 (1957).

[11] P.T. Wedepohl, "Influence of electron distribution on atomic interaction potentials", *Proc. Phys. Soc.*, **92**, 79 (1967).

[12] P.T. Wedepohl, "A simple analytical form of the Thomas-Fermi screening function and of Firsov's atomic interaction potentials", *J. Phys. B*, **1**, 307 (1968).

[13] A.A. Abrahamson, "Born-Mayer-type interaction potential for neutral ground-state atoms with Z = 2 to Z = 105", *Phys. Rev.*, **178**, 76 (1969).

[14] V.I. Gaydaenko and V.V. Nikulin, "Born-Mayer interatomic potential for atoms with Z = 2 to Z = 36, *Chem. Phys. Lett.*, **7**, 360 (1970).

[15] R.G. Gordon and Y.S. Kim, "Theory for the forces between closed-shell atoms and molecules", *J. Chem. Phys.*, **56**, 3122 (1972).

[16] Y.S. Kim and R.G. Gordon, "Study of the electron gas approximation", *J. Chem. Phys.*, **60**, 1842 (1974).

[17] Y.S. Kim and R.G. Gordon, "Ion-ion interaction potentials and their application to the theory of alkali halide and alkaline earth dihalide molecules", *J. Chem. Phys.*, **60**, 4332 (1974).
[18] Y.S. Kim and R.G. Gordon, "Unified theory for the intermolecular forces between closed shell atoms and ions", *J. Chem. Phys.*, **61**, 1 (1974).
[19] Y.S. Kim and R.G. Gordon, "Theory of binding of ionic crystals: Application to alkali-halide and alkaline-earth-diahalide crystals", *Phys. Rev. B*, **9**, 3548 (1974).
[20] A.J. Cohen and R.G. Gordon, "Theory of the lattice energy, equilibrium structure, elastic constants, and pressure-induced phase transitions in alkali-halide crystals", *Phys. Rev. B*, **12**, 3228 (1975).
[21] A.J. Cohen and R.G. Gordon, "Modified electron-gas study of the stability, elastic properties and high-pressure behaviour of MgO and CaO crystals", *Phys. Rev. B*, **14**, 4593 (1976).
[22] S. Trugman and R.G. Gordon, "Calculation of the energies, geometries and vibration frequencies of the alkali halide dimers", *J. Chem. Phys.*, **64**, 4625 (1976).
[23] M.J. Clugston and R.G. Gordon, "Electron-gas model for open shell-closed shell interactions. I. Application to the emission spectra of the diatomic noble-gas halides", *J. Chem. Phys.*, **66**, 239 (1977).
[24] M.J. Clugston and R.G. Gordon, "Electron-gas model for open shell-closed interactions. II. Application to the alkali monoxides", *J. Chem. Phys.*, **66**, 244 (1977).
[25] M. Waldman and R.G. Gordon, "Scaled electron gas approximation for intermolecular forces", *J. Chem. Phys.*, **71**, 1325 (1979).
[26] M. Waldman and R.G. Gordon, "Generalized electron gas Drude model theory of intermolecular forces", *J. Chem. Phys.*, **71**, 1340 (1979).
[27] E.K. Pearson and R.G. Gordon, "Local asymptotic gradient corrections to the energy functional of an electron gas", *J. Chem. Phys.*, **82**, 881 (1985).
[28] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas", *Phys. Rev.*, **136**, 864 (1964).
[29] See, for example: S. Lundqvist and N.H. March (editors), *Theory of the inhomogeneous electron gas*, Plenum, New York, 1983.
[30] K.A. Bruekner and J.D. Perez, "Convergence of the density gradient expansion for atoms", *Phys. Rev. A*, **2**, 2161 (1970).
[31] W.J. Carr, R.A. Coldwell-Horsfall and A.E. Fein, "Anharmonic contribution to the energy of a dilute electron gas - interpolation for the correlation energy", *Phys. Rev.*, **124**, 747 (1961).
[32] W.J. Carr and A.A. Maradudin, "Ground-state energy of a high density electron gas", *Phys. Rev.*, **133**, 371 (1964).
[33] W.C. Mackrodt and R.F. Stewart, "Defect properties of ionic solids: II Point defect energies based on modified electron-gas potentials", *J. Phys. C*, **12**, 431 (1979).
[34] A.I.M. Rae, "A theory for the interactions between closed shell systems", *Chem. Phys. Lett.*, **18**, 574 (1973).
[35] See, for example: G.L. Oliver and J.P. Perdew, "Spin-density gradient expansion for the kinetic energy", *Phys. Rev. A*, **20**, 387 (1979).
[36] See, for example: N. L. Allan and W.C. Mackrodt, "Calculated lattice and dynamic properties and defect chemistry of ternary and quaternary cuprates related to high-T_C superconductivity", *J. Chem. Soc., Faraday Trans. 2*, **85**, 385 (1989).
[37] N.L. Allan, D.T. Kulp and W.C. Mackrodt, "Atomistic simulation of some ternary inorganic fluorides", *J. Fluorine Chem.*, **45**, 188 (1989).
[38] P.T. Wedepohl, "Hybrid Thomas-Fermi-Dirac method for calculating atomic interaction energies: I. Theory", *J. Phys. C*, **10**, 1855 (1977).
[39] P.T. Wedepohl, "Hybrid Thomas-Fermi-Dirac method for calculating atomic interaction energies: II. Results and comparison with experimental data", *J. Phys. C*, **10**, 1865 (1977).
[40] S.C. Keeton and W.D. Wilson, "Vacancies, interstitials and rare gases in fluorite structures", *Phys. Rev. B*, **7**, 834 (1973).
[41] G.J. Dienes, D.O. Welch, C.R. Fischer, R.D. Hatcher, O. Lazareth, and M. Samberg, "Shell-model calculation of some point-defect properties in α-Al_2O_3", *Phys. Rev. B*, **11**, 3060 (1975).
[42] C.R.A. Catlow and M.J. Norgett, "Shell model calculations of the energies of formation of point defects in alkaline earth fluorides", *J. Phys. C*, **6**, 1325 (1973).
[43] C.R.A. Catlow, M.J. Norgett and T.A. Ross, "Ion transport and interatomic potentials in the alkaline-earth-fluoride crystals", *J. Phys. C*, **10**, 1627 (1977).
[44] B.G. Dick and A.W. Overhauser, "Theory of dielectric constants of alkali halide crystals", *Phys. Rev.*, **112**, 90 (1958).
[45] See, for example: W.C. Mackrodt, "Theory of defect calculations for ionic and semi-ionic materials", in *Mass Transport in Solids*, F. Beniere and C.R.A. Catlow, eds, Plenum Press, New York, 1983, Ch. 5.

[46] C.R.A. Catlow, "Defects in solid fluorides", in *Inorganic Solid Fluorides - Chemistry and Physics*, P. Hagenmuller, ed, Academic Press, London, 1985, Ch. 5.
[47] W.C. Mackrodt, "Defect calculations for ionic materials", in *Computer Simulation of Solids*, C.R.A. Catlow and W.C. Mackrodt, eds, Springer-Verlag, Berlin, 1982, Ch. 12.
[48] W.C. Mackrodt, "Defect energetics and their relation to non-stoichiometry in oxides", *Solid State Ionics*, **12**, 175 (1984).
[49] C.R.A. Catlow, I.D. Faux and M.J. Norgett, "Shell and breathing shell model calculations for defect formation energies and volumes in magnesium oxide", *J. Phys. C*, **9**, 419 (1976).
[50] J. Kendrick and W.C. Mackrodt, "Interatomic potentials for ionic materials from first principles calculations", *Solid State Ionics*, **8**, 247 (1983).
[51] C.R.A. Catlow, R. James, W.C. Mackrodt and R.F. Stewart, "Defect energetics in α-Al_2O_3 and rutile TiO_2", *Phys. Rev. B*, **25**, 1006 (1982).
[52] N.L. Allan, D.L. Cooper, C.G. West, P.J. Grout, and N.H. March, "Local density approximations to moments of momentum of diatomic molecules with Hartree-Fock-Roothaan quality electron distributions", *J. Chem. Phys.*, **83**, 239 (1985).
[53] N.L. Allan and D.L. Cooper, "Momentum space properties and local density approximations in small molecules: a critical appraisal", *J. Chem. Phys.*, **84**, 5594 (1986).
[54] J. Lloyd and D. Pugh, "On the theory of intermolecular forces between inert gas atoms", *Chem. Phys. Lett.*, **26**, 281 (1974).
[55] A.I.M. Rae, "A calculation of the interaction between pairs of rare gas atoms", *Molec. Phys.*, **29**, 467 (1975).
[56] N.L. Allan and D.L. Cooper, "Local density approximations and momentum space properties in small molecules and ionic solids", *J. Chem. Soc., Faraday Trans. 2*, **83**, 1675 (1987).
[57] D.L. Cooper, J. Gerratt and M. Raimondi, "Modern valence bond theory", *Adv. in Chem. Phys.*, **69**, 319 (1987).
[58] D.L. Cooper, J. Gerratt and M. Raimondi, "The spin-coupled approach to electron structure", *Molecular Simulation* (this volume), and references therein.
[59] D.L. Cooper, J. Gerratt and M. Raimondi, "Potential energy surfaces for the reaction of B^+ (^1P,^3P) with H_2 using spin-coupled VB theory. Asymptotic regions of the surfaces", *Chem. Phys. Lett.*, **127**, 600 (1986).
[60] D.L. Cooper and N.L. Allan, "Bond formation in momentum space", *J. Chem. Soc. Faraday Trans. 2*, **83**, 449 (1987).
[61] J.S. Cohen and R.T. Pack, "Modified statistical method for intermolecular potentials. Combining rules for higher van der Waals coefficients", *J. Chem. Phys.*, **61**, 2372 (1974).
[62] R. McWeeny, "Present status of the correlation problem", in *The new world of quantum chemistry*, B. Pullman and R. Parr, eds, Reidel, Dordrecht, 1976, page 3.
[63] J. Lloyd and D. Pugh, "Some applications of a self-exchange corrected electron gas model for intermolecular forces", *J. Chem. Soc. Faraday Trans. 2*, **73**, 234 (1977).
[64] G. Brual and S.M. Rothstein, "Rare gas interactions using an improved statistical method", *J. Chem. Phys.*, **69**, 1177 (1978).
[65] G. Brual and S.M. Rothstein, "H atom - rare gas interaction potentials from an electron gas model", *Chem. Phys. Lett.*, **61**, 167 (1979).
[66] S. Lee and Y.S. Yim, "Study of the Ar-N_2 interaction. II. Modification of the electron gas model potential at intermediate and large distances", *J. Chem. Phys.*, **70**, 4856 (1979).
[67] P.K.L. Drude, *The theory of optics*, Longmans-Green, London, 1933.
[68] J. Robles and G. Kemister, "Is correlation energy proportional to exchange energy?", *Chem. Phys. Lett.*, **134**, 27 (1987).
[69] E.H. Lieb and B. Simon, "Thomas-Fermi theory revisited", *Phys. Rev. Lett.*, **31**, 681 (1973).
[70] C.C. Shih, "Inhomogeneity corrections to the Thomas-Fermi-Dirac model of rare-gas diatomic systems", *Molec. Phys.*, **38**, 1225 (1979).
[71] D.R. Murphy, "Sixth-order-term of the gradient expansion of the kinetic-energy density functional", *Phys. Rev. A*, **24**, 1682 (1981).
[72] J.R. Chelikowsky, "Cohesive energies of simple metals as determined from atomic kinetic energies", *Phys. Rev. Lett.*, **47**, 387 (1981).
[73] E. Teller, "On the stability of molecules in Thomas-Fermi theory", *Rev. Mod. Phys.*, **34**, 627 (1962).
[74] E.A. Colbourn and W.C. Mackrodt, "The calculated defect structure of thoria", *J. Nucl. Mater.*, **118**, 50 (1983).
[75] W.C. Mackrodt and P.M. Woodrow, "Theoretical estimates of point defect energies in cubic zirconia", *J. Am. Ceram. Soc.*, **69**, 277 (1986).
[76] R. Car and M. Parrinello, "Unified approach for molecular dynamics and density-functional theory", *Phys. Rev. Lett.*, **55**, 2471 (1985).
[77] W. Kolos and E. Radzio, "Application of the statistical method in the theory of intermolecular interactions", *Int. J. Quant. Chem.*, **13**, 627 (1978).