The influence of improved dipole–quadrupole dispersion coefficients on the predicted cohesion of ionic oxides

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Abstract. The coefficients governing the dipole–quadrupole dispersive attractions between all the ions in solid magnesium oxide are computed *ab initio* using the coupled Hartree–Fock method. These confirm for oxides the previous conclusion that the Starkschall–Gordon formula provides the most reliable values for systems not amendable to *ab initio* computation.

Combination of the *ab initio* results with semiempirical estimates of the much smaller contributions from electron correlation produces improved coefficients. The cohesion predicted for MgO with the fully ionic model remains essentially unchanged on replacing the Starkschall–Gordon dipole–quadrupole dispersion coefficients with the improved values.

The use of improved predictions for $C_8(O^{2-} \ldots O^{2-})$ in solid CaO, ThO$_2$ and UO$_2$ in place of Starkschall–Gordon values leaves essentially unchanged the cohesion predicted for CaO whilst very slightly but significantly increasing that predicted for ThO$_2$ and UO$_2$. Theory and experiment for ThO$_2$ then agree as excellently as for MgO and CaO, thus showing no evidence for any covalency.

1. Motivation

Many different reasons motivate theoretical studies of polar solids by non-empirical techniques [1–3]. A wide variety of oxides are important both scientifically and technologically. Thus MgO and CaO are ceramics [4] that are also of geophysical interest as major constituents of the mantle of the earth [5–9]. The oxides of the group IV elements are also of interest as ceramics [4, 10, 11] whilst ThO$_2$ is important not only as a nuclear material but also as a solid state electrolyte and for its use in fluorescent tubes. The dioxides of uranium and plutonium are of interest as reactor fuels [12, 13]. The electronic structures and cohesive properties of several of these oxides have been investigated theoretically [2, 14–16] using a model [2, 14, 17, 18] fully ionic in the sense that the electronic wavefunction for the entire crystal is written as an antisymmetrized product of individual ion wavefunctions, each of which is optimal for the crystalline environment, subject to the constraints that each ion both contains a fixed integral number of electrons and retains the same symmetry as that of the free ion. This approach yields the total crystal energy as the sum of an uncorrelated contribution, computed using the relativistic integrals programme (RIP) [19, 20], augmented by corrections originating from electron correlation. The RIP computations, which take full account of the relativistic effects important for ions of high atomic number by use of the Dirac Hamiltonian [21], yield results that are exact once given the individual ion wavefunctions; these are optimized variationally taking into account the modification of the anion wavefunctions by their in-crystal environment [14, 18]. The correlation corrections are decomposed [2, 3, 14] into the long-range dispersive attractions [22, 23] between the ions plus the short-range terms, which are evaluated from the density functional theory [24] of

an electron gas of uniform density using the optimal wavefunctions generated in the RIP computations. This paper is concerned with the evaluation of one portion of the dispersion energy, in particular with the testing of an approximation to be invoked unless the crystal contains only ions of very low atomic number.

The dispersive or Van der Waals interaction between two ions arises from the attraction between the electric multipole induced on one ion by an electric multipole instantaneously present on the other [22, 23]. The case where both these multipoles are electric dipoles yields the leading contribution to the dispersive attraction, which is governed by the C_6 or dipole–dipole dispersion coefficient. These coefficients do not need to be considered here because it has been shown [2, 25] that they can be reliably derived to an accuracy of at least 5% through an appropriate use of the Slater–Kirkwood [26] formula. The next leading contribution to the dispersive attraction is the dipole–quadrupole term, which arises when one of the multipoles is an electric dipole with the other being an electric quadrupole. The evaluation of the dipole–quadrupole or C_8 dispersion coefficient governing such interactions is not on quite such a firm footing as that of the C_6 coefficients. Thus, excepting the case of a few halides containing only ions of very low atomic number [3, 27], these coefficients have had to be evaluated using the Starkschall–Gordon formula [28], which has been shown [2, 27] to be less accurate than the Slater–Kirkwood formula. It has been shown that the former usually underestimates the C_8 coefficient by about 15% but that this underestimation can occasionally reach 30% [2, 27]. The O^{2-} ion is much more affected than a halide ion by its interaction with the crystalline environment, owing its very existence solely to this interaction. This raises the possibility that the Starkschall–Gordon formula might be less accurate for crystals containing O^{2-} ions.

This paper has three objectives. The first is to test the accuracy of the Starkschall–Gordon formula by comparing its predictions for the C_8 coefficients in solid MgO with values derived from *ab initio* quantum chemistry computations. The second objective is to determine the effect on the predicted cohesive properties of solid MgO of replacing the previous C_8 coefficients derived from the Starkschall–Gordon formula with the more accurate values derived in this paper. The third objective is to use the new C_8 coefficient for the $O^{2-} \ldots O^{2-}$ interaction in MgO to derive more accurate values for the corresponding C_8 coefficients in CaO, ThO_2 and UO_2 and to determine the influence on the predicted cohesive properties of using these improved values.

2. *Ab initio* dipole–quadrupole dispersion coefficients for solid MgO

For the pair of ions R and S, the dipole–quadrupole dispersion coefficient $C_8(RS)$ is the sum

$$C_8(RS) = C_8^{DQ}(RS) + C_8^{QD}(RS) \tag{2.1}$$

where the contribution $C_8^{DQ}(RS)$ originates from the attraction between the quadrupole induced on ion S by a dipole instantaneously present on ion R [23, 29]. The quantity $C_8^{QD}(RS)$ similarly governs the attraction resulting from the interaction between the quadrupole induced on ion R by a dipole instantaneously present on ion S. In the case of two like ions (R = S), the coefficient $C_8(RS)$ is still given by (2.1) even though the two contributions $C_8^{DQ}(RS)$ and $C_8^{QD}(RS)$ are then identical. Both contributions in (2.1) can be exactly expressed as [29]

$$C_8^{DQ}(RS) = (15/\pi) \int_0^\infty \alpha^{(R)}(i\omega) C^{(S)}(i\omega) \, d\omega \tag{2.2a}$$

$$C_8^{QD}(RS) = (15/\pi) \int_0^\infty C^{(R)}(i\omega)\alpha^{(S)}(i\omega)\,d\omega \qquad (2.2b)$$

where $\alpha^{(R)}(i\omega)$ and $C^{(R)}(i\omega)$ are respectively the dipole and quadrupole polarizabilities of ion R at the imaginary frequency ω with $\alpha^{(S)}(i\omega)$ and $C^{(S)}(i\omega)$ being the corresponding quantities for ion S. For each ion, the nucleus of that ion is the origin with respect to which the quadrupole polarizability is defined. Although frequency-dependent dipole polarizabilities are origin independent, the frequency-dependent quadrupole polarizability of an ion depends on the choice of origin. The relations (2.2) are correct, yielding the unique and origin-independent dipole–quadrupole dispersion coefficients, only with the stated definition of each $C^{(R)}(i\omega)$ in which the nucleus of ion R is taken as origin. The results (2.2) permit $C_8^{DQ}(RS)$ and $C_8^{QD}(RS)$ to be predicted *ab initio* using quantum chemistry techniques since these can be used to compute both the dipole and quadrupole polarizabilities as a function of imaginary frequency. Here the CADPAC programme [30] is used to compute from coupled Hartree–Fock (CHF) theory the $C_8(RS)$ coefficients for all the pairs of ions in solid MgO with the final integrations in (2.2) being performed using the methods described elsewhere [31].

For small tightly bound cations such as Mg^{2+} there is abundant evidence that both the static dipole ($\alpha = \alpha(i0)$) and static quadrupole ($C = C(i0)$) polarizabilities as well as those at finite imaginary frequencies are unaffected by the crystalline environment, remaining the same as for the free isolated cation [25, 32–35]. Consequently the Mg^{2+} polarizabilities required in (2.2) were computed for an isolated cation. Although the quadrupole polarizability is a tensor having four suffices, each of which, p, q, r and s, can be x, y, or z, this tensor is spherically symmetric for an isolated closed shell system (R) with the components $C_{pq,rs}^{(R)}(i\omega)$ related to the spherical average $C^{(R)}(i\omega)$ through [29]

$$C_{pq,rs}^{(R)}(i\omega) = C^{(R)}(i\omega)[\tfrac{1}{2}(\delta_{pr}\delta_{qs} + \delta_{ps}\delta_{qr}) - \tfrac{1}{3}\delta_{pq}\delta_{rs}]. \qquad (2.3)$$

The basis set required for the CADPAC computations was an uncontracted 12s8p5d4f set of Gaussian functions constructed by augmenting the 12s8p5d basis set previously used to study the dipole polarizabilities [34] and C_6 dispersion coefficients [25] in solid MgO with four sets of f functions whose exponents were equal to those of the four most diffuse d functions. This basis is validated by the close agreement between our CADPAC CHF prediction of 0.5181 au for the quadrupole polarizability $\alpha^{(2)}$ ($= 2C(i0)$) with the value of 0.5198 au derived [36] from a computation in which the CHF equations were solved using numerical techniques.

The crucial interactions between an O^{2-} ion and its in-crystal environment were simulated by the now well proven method [25, 27, 32–34] of performing a CHF computation for a cluster containing one O^{2-} ion plus its six closest Mg^{2+} neighbours including all their electrons with the entire cluster being embedded in a $5 \times 5 \times 5$ fragment of the point charge representation of the remainder of the lattice. The outermost charges of this fragment were scaled so as to reproduce the correct electrostatic potential at the nucleus of the O^{2-} ion whilst maintaining the overall electrical neutrality of the entire system. A large basis set was used for the O^{2-} ion whilst each Mg^{2+} ion in the embedded cluster was described by a minimal [2s1p] contraction consisting of the occupied orbitals generated by an SCF computation for a free Mg^{2+} ion using a 10s8p subset of the full Mg^{2+} basis. This contracted cation basis provides an excellent representation of Mg^{2+} charge distribution, thereby providing a good model for the important effects of overlap on the properties of an in-crystal O^{2-} ion. The origin is taken at the O^{2-} nucleus in the cluster computation, which yields

the frequency-dependent dipole ($\alpha^{CLUS}(i\omega)$) and quadrupole ($C_{pq,rs}^{CLUS}(i\omega)$) polarizabilities of the entire cluster. The frequency dependent polarizabilities of the O^{2-} ion have then to be derived by subtracting both the multipole-induced multipole corrections and the predictions of the cation frequency-dependent polarizabilities yielded by this basis set with this choice of origin. Both the dipole and quadrupole frequency-dependent polarizabilities of each cation are predicted to be zero if just the contracted minimal [2s1p] basis of that cation is used and the origin is taken at the cation nucleus. In the cluster calculation, non-zero values for such cation polarizabilities arise through basis set superposition effects originating from the presence of the anion basis functions. Further cation contributions to the $C_{pq,rs}^{CLUS}(i\omega)$ arise because the origin in the cluster computation is taken at the anion nucleus rather than at any cation nucleus. The sums of these cation contributions to $C_{pq,rs}^{CLUS}(i\omega)$ and the basis superposition contributions to the cluster dipole and quadrupole polarizabilities were generated by performing a CHF computation for just the cage of six Mg^{2+} ions including all their 60 electrons embedded in the point charge lattice. The same contracted Mg^{2+} basis plus the entire O^{2-} basis were used but the anion nucleus and electrons were replaced by a point charge of size -2 au. Since the resulting dipole ($\alpha^{CAGE}(i\omega)$) and the quadrupole ($C_{pq,rs}^{CAGE}(i\omega)$) polarizabilities contain both these cation contributions, the required anion ($R = A$) dipole ($\alpha^{(A)}(i\omega)$) and quadrupole ($C_{pq,rs}^{(A)}(i\omega)$) polarizabilities were calculated from

$$\alpha^{(A)}(i\omega) = \alpha^{CLUS}(i\omega) - \alpha^{CAGE}(i\omega) \tag{2.4a}$$

$$C_{pq,rs}^{(A)}(i\omega) = C_{pq,rs}^{CLUS}(i\omega) - C_{pq,rs}^{CAGE}(i\omega). \tag{2.4b}$$

For a closed shell ion located at a site of octahedral symmetry $\alpha^{(A)}(i\omega)$ remains isotropic whilst the spherical average of the anion quadrupole polarizability required in (2.2) is given by [29]

$$C^{(A)}(i\omega) = \tfrac{3}{5}[C_{xx,xx}^{(A)}(i\omega) + 2C_{xy,xy}^{(A)}(i\omega)]. \tag{2.5}$$

In all the *ab initio* computations for both the cluster and cage, the distance between an O^{2-} ion and its six closest Mg^{2+} neighbours was taken to have the value of 3.796 au, which was experimentally determined as the equilibrium cation-anion separation at 0 K [37]. Two different large basis sets for the O^{2-} ion were used, the first being a 14s9p5d4f set constructed by augmenting the 14s9p5d set used [25, 34] to study the dipole polarizability and dipole–dipole dispersion coefficients with four sets of f functions having exponents equal to those of the four most diffuse sets of d functions. The second O^{2-} basis was a 15s10p6d5f set generated by adding for each symmetry a single more diffuse set with exponents generated by geometrical progression from the two most diffuse functions of the same symmetry in the first basis set. Computations performed using the first of these two basis sets predicted the static dipole ($\alpha^{CLUS} = \alpha^{CLUS}(i0)$) and spherically averaged quadrupole polarizabilities ($C^{CLUS} = C^{CLUS}(i0)$) of the cluster to be 11.203 au and 32.364 au respectively. Use of the second and augmented basis yielded the essentially identical results of 11.211 au and 32.491 au, thereby confirming the excellence of the first basis, which was therefore used in all the remaining computations. The static dipole polarizability of the cage was found to be 0.461 au, thereby predicting through (2.4) an in-crystal O^{2-} polarizability of 10.741 au. The very small difference from the previous *ab initio* CHF prediction of 10.957 au [34] is attributable to the absence of the basis functions of f symmetry in the earlier computation. The *ab initio* value of 6.596 au for the spherically averaged quadrupole polarizability of the cage predicts through (2.4) that the static quadrupole polarizability

$(C^{(A)}(i0))$ of an O^{2-} ion in an MgO crystal at its equilibrium geometry is 25.768 au. Both these anion and cage polarizabilities are very similar to the previous *ab initio* CHF predictions [38] of 26.049 au and 25.756 au for $C^{(A)}(i0)$ and 6.109 au and 6.408 au for the spherically averaged cage quadrupole polarizability. The previous computations [38] differed from ours both in that the previous basis contained one less function of f symmetry and in that two slightly different methods were used to extract the desired anion polarizability from that of the cluster. The extremely close agreement between all three sets of results is strong evidence for the reliability of all these computations.

Table 1. A comparison of *ab initio* CHF and Starkschall–Gordon C_8(RS) coefficients for MgO (au).

Method	C_8^{DQ}(CA)	C_8^{QD}(CA)	C_8(AA)	C_8(CC)
CHF[a]	55.252	12.081	1411.994	3.153
SG[b]	41.628	8.631	1089.238	2.223

[a] CHF, predictions of *ab initio* CHF computations.
[b] SG, corresponding predictions of the Starkschall–Gordon formula (3.1) derived from the *ab initio* CHF results of table 2 for the C_6(RS) coefficients and 2p orbital radial expectation values computed from the free Mg^{2+} Hartree–Fock wavefunction and in-crystal O^{2-} wavefunction computed using the OEMFS environmental model. For Mg^{2+} $\langle r^2 \rangle = 3.528$ au and $\langle r^4 \rangle = 4.685$ au and for O^{2-} $\langle r^2 \rangle = 17.324$ au and $\langle r^4 \rangle = 110.956$ au.

For all three types of ion pair in MgO, table 1 presents the dipole–quadrupole dispersion coefficients calculated through (2.2) from the frequency-dependent dipole and quadrupole polarizabilities computed *ab initio* at the CHF level. The values, the first entirely new results to be presented here, will be considerably more accurate than the previous estimates of the coefficients derived from the Starkschall–Gordon formula.

3. Test of the Starkschall–Gordon formula

The Starkschall–Gordon formula [28], an approximation derived by making a clever choice for the average energy in a sum over states perturbation theory expression for the dispersion energy, relates the C_8^{DQ}(RS) coefficient to the corresponding dipole–dipole dispersion coefficient C_6(RS) through

$$C_8^{DQ}(RS) = \tfrac{3}{2} C_6(RS) \langle r^4 \rangle_S / \langle r^2 \rangle_S \tag{3.1a}$$

$$C_8^{QD}(RS) = \tfrac{3}{2} C_6(RS) \langle r^4 \rangle_R / \langle r^2 \rangle_R. \tag{3.1b}$$

Here $\langle r^n \rangle_R$ is for all the electrons belonging to ion R the expectation value of the nth power of their distance from the nucleus of ion R with $\langle r^n \rangle_S$ being the corresponding quantity for ion S. This presentation of the Starkschall–Gordon formula implies that all the electrons belonging to a given ion should be included in the evaluation of the expectation values $\langle r^4 \rangle_S$ and $\langle r^2 \rangle_S$. However since the inner electrons make only negligible contributions to both the static polarizabilities and polarizabilities at imaginary frequency whose integrals (2.2) yield exactly the dipole–quadrupole dispersion coefficients, it would be illogical to include the contribution of these inner electrons in the evaluation of the expectation values in (3.1). Indeed numerical tests of the accuracy of (3.1) for both pairs of inert gases as well as for pairs of isoelectronic cations and halide ions in ionic solids showed [2, 27] that the inclusion

of all the electrons in the evaluation of the $\langle r^n \rangle_R$ significantly degraded the quality of the predictions and that consideration of only the six outermost p electrons yielded significantly *more accurate results. Hence only these six outermost electrons will be considered in* (3.1) in the tests to be presented here. The Starkschall–Gordon formula is of interest because it provides the only method of deriving realistic values for dipole–quadrupole coefficients not amenable to *ab initio* computation because either the in-crystal ions contain too many electrons or have nuclear charge so high that relativistic effects become important.

Investigation of the accuracy with which (3.1) can reproduce the *ab initio* CHF predictions of the dipole–quadrupole dispersion coefficients requires that one uses in (3.1) $C_6(RS)$ dispersion coefficients computed in the same CHF approximation. The latter are calculated from the relation [29, 39]

$$C_6(RS) = (3/\pi) \int_0^\infty \alpha^{(R)}(i\omega)\alpha^{(S)}(i\omega)\,d\omega \tag{3.2}$$

using as input the same *ab initio* CHF dipole polarizabilities $\alpha^{(R)}(i\omega)$ that were used as input to (2.2). For the ion pairs in MgO, the resulting CHF $C_6(RS)$ coefficients presented in table 2 are, as expected, very similar to those previously computed [25] using a basis set lacking functions of f symmetry. For a free Mg^{2+} ion, the expectation values in (3.2) were evaluated from the numerical Hartree–Fock wavefunction computed using the Oxford atomic Dirac–Fock programme [40] with an artificially large value for the velocity of light. For closed shell systems such computations reproduce exactly [41, 42] the results of conventional non-relativistic calculations. The corresponding expectation values for the in-crystal O^{2-} ion were evaluated from an ion wavefunction computed by including in the Dirac–Fock programme the currently most reliable model, the OEMFS model [14, 18], for the important interaction between each anion electron and the in-crystal environment. These techniques had to be used because the CADPAC program does not compute the $\langle r^4 \rangle_R$ expectation values.

Table 2. Currently recommended values for dipole–quadrupole dispersion coefficients in MgO (au).

	$Mg^{2+}\dots O^{2-}$		$O^{2-}\dots O^{2-}$	$Mg^{2+}\dots Mg^{2+}$
$C_6^{CHF}(RS)$[a]	4.333		56.689	0.558
$C_6^{BEST}(RS)$[b]	4.292		60.491	0.536
$C_8^{BEST}(RS)$[c]	54.729 (DQ)	11.967 (QD)	1506.693	3.029

[a] Present *ab initio* CHF result.
[b] Best value for the $C_6(RS)$ coefficient derived [2] through the Slater–Kirkwood formula from best and experimentally derived values for the ionic polarizabilities.
[c] Best currently available values for dipole–quadrupole dispersion coefficients derived through (4.1) from the $C_6^{CHF}(RS)$ and $C_6^{BEST}(RS)$ values of this table and the CHF $C_8(RS)$ results in table 1.

Table 1 reports the predictions for the *ab initio* CHF dipole–quadrupole dispersion coefficients provided by the Starkschall–Gordon formula when the *ab initio* $C_6(RS)$ coefficients are used as input. The results show that this formula underestimates all the C_8 coefficients by at least 23% with the largest errors of 29% occurring for $C_8(Mg^{2+}\dots Mg^{2+})$ and $C_8^{QD}(Mg^{2+}\dots O^{2-})$. These errors are greater than the 10–20% underestimations found [2, 27] for the inert gas atoms, cations or halide ions excepting the case of $C_8(Na^+\dots Na^+)$, for which the Starkschall–Gordon prediction is 30% too small. Inclusion of the 1s core electrons in the evaluation of the expectation values in the Starkschall–Gordon formula would increase the discrepancies for MgO because $\langle r^2 \rangle$ for a 1s core orbital is larger than $\langle r^4 \rangle$ for such an orbital.

4. Improved dipole-quadrupole dispersion coefficients and the cohesion of MgO

The cohesion of solid MgO has been previously computed [2, 14] by augmenting the uncorrelated contributions calculated using the RIP program with the energies originating from dispersion and short-range electron correlation. These computations used the best values of the dipole–quadrupole dispersion coefficients that were then available. Although these were derived from the Starkschall–Gordon formula, they differ slightly from the Starkschall–Gordon predictions of table 1. These previous best values [2, 14] were derived by using as input to (3.1) not the CHF $C_6(RS)$ coefficients but the best values available for the $C_6(RS)$ coefficients, which are those, labelled $C_6^{BEST}(RS)$ in table 2, derived using the Slater–Kirkwood formula from experimental polarizability data. Electron correlation effects cause the true values of the $C_6(RS)$ coefficients to differ from the predictions of *ab initio* CHF theory. The first column of table 3 shows that for solid MgO the lattice energy D_e, closest equilibrium cation–anion separation (R_e) and bulk compressibility (B) predicted from the computations using the previous Starkschall–Gordon dipole–quadrupole dispersion coefficients agree well with the experimental values reported in the last column of table 3. It should be stressed that in calculating the dispersion energy it was essential to take account of the damping [2, 22, 43] of its standard form in which the leading or dipole–dipole dispersive attraction between two ions varies as the inverse sixth power of their separation. This damping, which reduces the magnitude of the undamped dispersion energy when the overlap of the wavefunctions of the two interacting species is not negligible, was incorporated using the previous described method [2, 14] based on the theory of Jacobi and Csanak [43].

Table 3. The dependence of the predictions of MgO cohesion on the $C_8(RS)$ coefficients. Lattice energy D_e in kJ mol^{-1} is for the process of converting solid into free cations, free O$^-$ ions and free electrons; R_e is the closest equilibrium cation-anion separation in au; B is the bulk compressibility in 10^{10} N m^{-2}. All predictions are derived using equation (2.4) of [14] expressing the crystal cohesion as a sum of an uncorrelated part computed using the RIP program augmented by short-range correlation terms computed using the density functional theory [24] of a uniform electron gas plus dipole–dipole and dipole–quadrupole dispersive attractions evaluated including their damping arising from overlap of the wavefunctions of the interacting ions. The O^{2-} ion wavefunction is computed using the OEMFS environmental method. Calculations differ only in the values used for the dipole–quadrupole $C_8(RS)$ dispersion coefficients: SG, previous predictions from [14] using $C_8(RS)$ from the Starkschall–Gordon formula using the best $C_6(RS)$ coefficients presented in table 2; CHF, predictions using *ab initio* CHF coefficients of table 2; Best, using the best current values of table 2.

	SG	CHF	Best	Experiment[a]
D_e	3038	3042	3043	3038
R_e	3.994	3.990	3.990	3.979
B	19.92	20.00	20.02	17.9

[a] Experimental values: D_e from [6], R_e from [37] and B the average of the three values from [47].

A calculation differing from that previously reported [14] only through the use of the present *ab initio* CHF predictions for the dipole–quadrupole dispersion coefficients predicts (second column of table 3) a slightly greater crystal cohesion as manifested by slightly greater D_e, slightly smaller R_e and larger B value because the *ab initio* CHF predictions for the dipole-quadrupole dispersion coefficients are greater than the previous values [14]

derived using the Starkschall–Gordon formula. However although all these CHF dipole–quadrupole dispersion coefficients are at least 23% larger than the previous Starkschall–Gordon values, the predicted crystal cohesion remains essentially unchanged because the dipole–quadrupole terms only constitute about a third of the total dispersion energy, which is itself only about 2% of the total lattice energy of 3038 kJ mol^{-1} [6]. Thus the dipole–quadrupole dispersive attractions contribute only some 19 kJ mol^{-1} to this lattice energy.

The discrepancies of some 25% between the *ab initio* CHF predictions for the dipole–quadrupole dispersion coefficients and the corresponding Starkschall–Gordon results show that the *ab initio* CHF values will be considerably more accurate than the previously used [2, 14] Starkschall–Gordon predictions even though electron correlation effects are absent from CHF theory. There is some evidence [27] that electron correlation produces the same fractional change in the dipole–quadrupole dispersion coefficient as it generates in the corresponding dipole–dipole dispersion coefficient. In this event values $(C_8^{BEST}(RS))$ of dipole–quadrupole dispersion coefficients more accurate than those $(C_8^{CHF}(RS))$ of *ab initio* CHF computations can be derived using the relation

$$C_8^{BEST}(RS) = C_8^{CHF}(RS)[C_6^{BEST}(RS)/C_6^{CHF}(RS)] \qquad (4.1)$$

where $C_6^{BEST}(RS)$ and $C_6^{CHF}(RS)$ are respectively the best and *ab initio* CHF values for the corresponding dipole–dipole dispersion coefficient $C_6(RS)$. The best values currently available for the dipole–quadrupole dispersion coefficients in solid MgO are those reported in the last row of table 2, which were derived from (4.1) using the present CHF predictions for the dipole–quadrupole and dipole–dipole dispersion coefficients and the best current values (the second line of table 2) for the $C_6(RS)$ derived [2] using the Slater–Kirkwood formula. The resulting dipole–quadrupole dispersion coefficients are slightly less than the corresponding CHF values except for $C_8(O^{2-}\ldots O^{2-})$, which is some 6% greater than the CHF prediction. Even though the closest anion–anion separation is $\sqrt{2}$ times as large as the closest cation–anion separation, the $O^{2-}\ldots O^{2-}$ interactions contribute some two-thirds of the total dipole–quadrupole dispersion energy because $C_8(O^{2-}\ldots O^{2-})$ is so much greater than the other dipole–quadrupole dispersion coefficients. This explains why a slightly greater dispersion energy leading to slightly augmented crystal cohesion (table 3) is predicted when the CHF results for the dipole–quadrupole dispersion coefficients are replaced by the best current values assembled in the last line of table 2. However, since the dipole–quadrupole dispersive attractions constitute only a small fraction of the total crystal cohesive energy, the crystal properties predicted on using the present improved values for the dipole–quadrupole dispersion coefficients remain essentially unchanged from the previous results [14] derived using Starkschall–Gordon dipole–quadrupole dispersion coefficients.

5. Improved $C_8(O^{2-}\ldots O^{2-})$ coefficients and the cohesion of CaO, ThO$_2$ and UO$_2$

The best currently available estimate of 1506.693 au for $C_8(O^{2-}\ldots O^{2-})$ in MgO is significantly greater, by a factor of 1.296, than that of 1162.290 au [14] derived from the Starkschall–Gordon formula using the best currently available value for $C_6(O^{2-}\ldots O^{2-})$. This suggests that the Starkschall–Gordon estimates of $C_8(O^{2-}\ldots O^{2-})$ in CaO, ThO$_2$ and UO$_2$ used previously [14–16, 44] will similarly be underestimates. In MgO the value (60.491 au) of $C_6(O^{2-}\ldots O^{2-})$ is considerably smaller than in the other three oxides, for which this coefficient lies between 93 au and 103 au. This explains why the Starkschall–Gordon predictions of $C_8(O^{2-}\ldots O^{2-})$ in these three oxides are considerably greater than the corresponding value of 1162.290 au in MgO.

For an oxide of the metal M for which CHF results are unavailable, it has been pointed out [3] that a better estimate $(C_8^{MO}(O^{2-} \ldots O^{2-}))$ of $C_8(O^{2-} \ldots O^{2-})$ could be derived from an accurate value $(C_6^{MO}(O^{2-} \ldots O^{2-})$ of the corresponding dipole–dipole dispersion coefficient if the in-crystal environment caused the same fractional change in both $C_6(O^{2-} \ldots O^{2-})$ and $C_8(O^{2-} \ldots O^{2-})$. In this event one would have

$$C_8^{MO}(O^{2-} \ldots O^{2-}) = C_8^{MgO}(O^{2-} \ldots O^{2-})[C_6^{MO}(O^{2-} \ldots O^{2-})/C_6^{MgO}(O^{2-} \ldots O^{2-})]. \quad (5.1)$$

Substitution into this relation of the currently most trustworthy values of 1506.693 au and 60.491 au for $C_8(O^{2-} \ldots O^{2-})$ and $C_6(O^{2-} \ldots O^{2-})$ in MgO predicts $C_8(O^{2-} \ldots O^{2-})$ in CaO, ThO$_2$ and UO$_2$ to be 2546.217 au, 2371.041 au and 2337.764 au respectively by using the $C_6(O^{2-} \ldots O^{2-})$ coefficients derived in [14] for CaO and in [44] for ThO$_2$ and UO$_2$. These three new values for $C_8(O^{2-} \ldots O^{2-})$ are enhanced by no less than 45%, 68% and 65% respectively from the previously used Starkschall–Gordon predictions reported in table 4. Previous tests [2, 27] of the accuracy of the Starkschall–Gordon formula showed that this usually underestimated the dipole–quadrupole coefficient by between 10% and 15% and that this underestimation sometimes reached 30%. However since no accurate dipole–quadrupole dispersion coefficient has ever been found to be as much as 45%, still less 65%, greater than the Starkschall–Gordon prediction, the above values derived from (5.1) must be rejected.

Table 4. Starkschall–Gordon and recommended values for $C_8(O^{2-} \ldots O^{2-})$ for other oxides (au).

	CaO	ThO$_2$	UO$_2$
SG[a]	1752.438	1411.599	1420.599
Scaled SG[b]	2271.160	1829.432	1841.096

[a] Previous [14–16, 44] predictions of the Starkschall–Gordon formula derived from best and experimentally derived values for $C_6(RS)$ coefficients and expectation values calculated from in-crystal O^{2-} wavefunctions computed using the OEMFS environmental model.
[b] SG values scaled by the factor 1.296, which yields the best current value (table 3) for $C_8(O^{2-} \ldots O^{2-})$ from the previous [2] Starkschall–Gordon prediction.

Although the Starkschall–Gordon formula supports the idea that an environmentally induced increase of $C_6(O^{2-} \ldots O^{2-})$ will cause an enhancement of $C_8(O^{2-} \ldots O^{2-})$, this relation suggests that there are also other factors, which become expressed in the Starkschall–Gordon approximation through the ratio of the ground state expectation values. This ratio $\langle r^4 \rangle_A/\langle r^2 \rangle_A$ (A = O^{2-}) is considerably greater (6.405, see the footnote to table 1) for MgO than for CaO, ThO$_2$ and UO$_2$, where it takes the values 5.714, 4.943 and 5.045 respectively. The ratio for CaO is derived from the results $\langle r^4 \rangle_A = 94.651$ au and $\langle r^2 \rangle_A = 16.564$ au, whilst those for ThO$_2$ and UO$_2$ are calculated from the data in table 6 of [44]. The decrease of this ratio with increasing cation atomic number arises because the fractional reduction in $\langle r^4 \rangle_A$ (from 110.956 au in MgO to 74.841 au in ThO$_2$) is much greater than that of $\langle r^2 \rangle_A$ (from 17.324 au in MgO to 15.141 au in ThO$_2$). It would be expected that as the O^{2-} ion becomes increasingly compressed by its in-crystal environment that $\langle r^4 \rangle_A$ with its large contribution from outer spatial regions would be more greatly affected than $\langle r^2 \rangle_A$. These considerations pinpoint the theoretical inadequacies of (5.1) and suggest the environmental dependence of a given dipole–quadrupole dispersion coefficient would be better described by introducing into the Starkschall–Gordon formula a scaling factor, which should be expected

to be constant for a given type of ion pair. For $C_8(O^{2-}\dots O^{2-})$ in MgO comparison of the best current value of 1506.693 au for $C_8(O^{2-}\dots O^{2-})$ with the Starkschall–Gordon estimate of 1162.290 derived [2] from the best currently available value for $C_6(O^{2-}\dots O^{2-})$ shows this scaling factor to be 1.296. The best currently available values for $C_8(O^{2-}\dots O^{2-})$ in CaO, ThO$_2$ and UO$_2$ derived by introducing this scaling factor into (3.1) are assembled in the last line of table 4.

Table 5. Fully ionic model *ab initio* predictions of the cohesion of solid oxides (see notes a and b to table 3). Calculations differ only in the values used for the anion–anion dipole–quadrupole $C_8(O^{2-}\dots O^{2-})$ dispersion coefficients: SG, previous predictions from [14] (CaO), [15] (ThO$_2$) and [16] (UO$_2$) using the $C_8(O^{2-}\dots O^{2-})$ coefficients of the first line of table 4 derived from the Starkschall–Gordon formula using the best C_6(RS) coefficients; Scaled, derived using best current values (the second line of table 4) for $C_8(O^{2-}\dots O^{2-})$. ThO$_2$ predictions are very slightly different from those of [15] through use of the preferable method of Simons *et al* [48] of fitting the cohesive energies ($U_L(R)$) computed as a function of R. Experimental values: D_e for CaO from [6], ThO$_2$ from [15] and UO$_2$ from [16]; R_e for CaO at 0 K from [37], ThO$_2$ and UO$_2$ from [49]; B for CaO from [50], ThO$_2$ from [51] and UO$_2$ calculated from elastic constant data from [52] as $\frac{1}{3}(C_{11}+2C_{12})$.

	CaO			ThO$_2$			UO$_2$		
	SG	Scaled	Experiment	SG	Scaled	Experiment	SG	Scaled	Experiment
D_e	2645	2648	2644	8130	8140	8100	8282	8292	8362
R_e	4.536	4.531	4.537	4.596	4.587	4.582	4.532	4.525	4.474
B	11.66	11.69	11.3	18.46	18.41	19.3	23.32	23.38	21.3

In table 5 are reported the changes in the crystal cohesion of CaO, ThO$_2$ and UO$_2$ produced when the previous Starkschall–Gordon results for $C_8(O^{2-}\dots O^{2-})$ are replaced by the improved values just derived. Although the predictions [14] for CaO remain essentially unaltered, the computed value of the closest cation–anion separation for ThO$_2$ is slightly but significantly improved. The improvement in the values of $C_8(O^{2-}\dots O^{2-})$ affects the ThO$_2$ and UO$_2$ predictions more than those for the alkaline earth oxides because the $O^{2-}\dots O^{2-}$ separation in the fluorite structures of the former is $[2/\sqrt{3}]R$ compared with $(\sqrt{2})R$ in the rock salt structures of the latter. It should be noted that the experimental values for the lattice energies (D_e) of ThO$_2$ and UO$_2$ are not known so accurately as those of MgO and CaO because the Born–Haber cycles through which the two former were derived contain the experimentally unknown third and fourth cation ionization potentials. These potentials therefore had to be evaluated [15, 16] as the sum of an uncorrelated part computed using the Oxford atomic Dirac–Fock program [40] plus a semiempirical estimate of the smaller contributions from electron correlation. However with the introduction of the improved values for $C_8(O^{2-}\dots O^{2-})$, the agreement between theory and experiment is now as good for ThO$_2$ as for MgO and CaO. The conclusion considers the relevance of this result to discussions of any possible covalency in ThO$_2$.

6. Conclusion

The dipole–quadrupole dispersion coefficients for all the ion pairs in solid MgO at its experimental equilibrium geometry have been computed by using *ab initio* coupled Hartree–Fock theory. These results have been used to demonstrate that the predictions of these coefficients provided by the Starkschall–Gordon formula [28] show errors no greater than

the larger of those found previously [2, 27] for other ions. Thus the underestimations of these coefficients by the Starkschall–Gordon formula are no greater than 30%, which suggests that the predictions of this formula for any dipole–quadrupole dispersion coefficient involving an in-crystal O^{2-} ion will be no greater. This result is interesting because using the Starkschall–Gordon formula is currently the only method of deriving realistic values for those dipole–quadrupole coefficients not amenable to *ab initio* computation. Thus it has previously been shown [2] that other semiempirical methods for deriving dipole–quadrupole coefficients, such as the formulae of Margenau [45] and Narayan [46], are quite untrustworthy because they often yield results in error by several hundreds of per cent.

We have presented in the last line of table 2 the currently most reliable values for the dipole–quadrupole dispersion coefficients for all the ion pairs in MgO by combining the *ab initio* CHF predictions with semiempirical estimates of the much smaller contributions originating from electron correlation. Although the dipole–quadrupole dispersion energy computed for MgO using these improved coefficients is about 25% greater than that previously obtained using the Starkschall–Gordon dipole–quadrupole dispersion coefficients, the total dipole-quadrupole dispersion energy is a sufficiently small fraction of the total cohesive energy that use of the improved coefficients leaves the predicted cohesive properties of the crystal essentially unchanged, showing the same good agreement with experiment.

The comparison of our presently recommended value for $C_8(O^{2-} \ldots O^{2-})$ in MgO with the prediction from the Starkschall–Gordon formula enabled improved values to be derived for this coefficient in the other oxides CaO, ThO_2 UO_2 whose cohesive properties have been studied [14–16] within the fully ionic model by using the relativistic integrals program [18, 19]. Although the new coefficients are somewhat larger than the previous values, the cohesive properties of CaO predicted on introducing the improved value of $C_8(O^{2-} \ldots O^{2-})$ remained essentially unchanged, showing the same excellent agreement with experiment. The closer anion–anion separations in the fluorite structures of ThO_2 and UO_2 compared with those in the rock-salt-structured alkaline earth oxides caused the introduction of the improved values of $C_8(O^{2-} \ldots O^{2-})$ to predict a very slightly but significantly enhanced cohesion of ThO_2 and UO_2. For ThO_2 this enhancement brought the agreement between theory and experiment to the same excellent level enjoyed by the alkaline earth oxides. Thus the cohesive properties of ThO_2 can be reproduced by the fully ionic model with the consequence that these properties provide no evidence for covalency even though it is possible that the cohesive properties might be insensitive to deviations from full ionicity. The cohesive properties of ThO_2 are thus similar to those of MgO and CaO, which similarly provide no evidence for covalency [14].

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