Ab initio determination of the bulk properties of MgO

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Ab initio periodic Hartree-Fock (HF) theory was used to determine the elastic constants and selected phonon frequencies of bulk MgO; the accuracy of *a posteriori* correlation corrections to the periodic Hartree-Fock calculations is also discussed. Inclusion of diffuse atomic orbitals in the MgO basis was necessary to accurately describe elastic distortions and phonon vibrations of the solid. The computed HF lattice constant (4.195 Å) agrees with experiment (4.19 Å) and the elastic constants are within +15% of the observed values. Correlation corrections to these energetics shorten the lattice parameter to 4.09 Å and further stiffen the elastic constants. The HF phonon frequencies at the (Γ, X, and L) points in the Brillouin zone were within 15% of experiment and the correlation corrections softened the modes improving agreement with experiment. These data will be used to parametrize electrostatic shell models of MgO.

I. INTRODUCTION

This is the first in a series of papers that will discuss the derivation of electrostatic shell models from *ab initio* calculations of the bulk properties in selected classes of ionic and semi-ionic compounds. The motivation for the present work was to determine the level of *ab initio* theory needed to accurately describe bulk MgO. These data will, in turn, be used to parametrize the models. In recent years periodic Hartree-Fock (HF) theory has been used to study the bulk and surface properties of a wide range of ionic and semi-ionic systems.[1,2] The analytic representation of the HF operators in a local basis set allows one to perform numerically accurate calculations very efficiently. In general, the structural and elastic properties of these materials are well described; errors in lattice constants and elastic properties being +1-2% and +5-10%, respectively, which is in line with molecular experience.[3] In the current work we also examine the performance of *a posteriori* correlation corrections estimated using gradient-corrected density functionals (as implemented in the program CRYSTAL92).[4] We report the first calculations of this nature for the elastic constants and the high symmetry point phonon frequencies of MgO.

The relative accuracy of these methods and the sensitivity of the bulk properties to directional flexibility in the basis set are described below. The second paper in this series will compare computed energetics of the *ab initio* derived shell model with the its empirically derived counterpart.

Although it is practical to use *ab initio* theory to describe the bulk and surface properties of many materials, it may not be computationally efficient to use this method to predict the full structural relaxation that accompanies crystal cleavage or defect site formation. It is therefore beneficial to obtain structural information from simple models which can then be used as starting geometries for *ab initio* investigations of complex systems containing surfaces, defects, and compositional mixtures. Shell models have been used extensively to describe energetic and dynamical processes in solids. Traditionally, they have been constructed primarily from empirical data.[5-7] However, a recent study reported the derivation of a dipolar shell model for layered AB_2 compounds from periodic HF calculations on $MgCl_2$.[8-10] The empirical fitting procedure is obviously limited to those systems for which ample experimental results are available. The advantage of the *ab initio* derived models is that they can be used both to study systems that have not been probed by experiment and to describe the properties of idealized structures that do not exist in nature. The latter investigations help to determine the intersystem transferability of the derived models. The *ab initio* data also contain a description of anharmonic contributions to the distortion energetics. These are incorporated into the models by fitting the total-energy curves as a function of distortion parameter, not just the computed force constants. An accurate description of the energetics is essential if models derived for bulk solids are to be used to predict extensive structural perturbations due to changes in coordination and environment resulting from the formation of surfaces, interfaces, and site defects.

II. COMPUTATIONAL DETAILS

Periodic Hartree-Fock (HF) theory[1] as implemented in the program CRYSTAL92 (Ref. 4) was used in the present work in conjunction with *a posteriori* correlation-corrected periodic Hartree-Fock theory.[11,12] Correlation corrections to the ground-state periodic HF energies are made using three correlation-only density functionals—

TABLE I. MgO lattice parameter and elastic constants basis set dependence. Basis sets expressed as [Mg/O]. Experimental values from Anderson, 1966.

	Expt.	[8511/8411]	% error	[8511*/8411*]	% error
a (Å)	4.19	4.205	(+0.36)	4.195	(+0.1)
B (GPa)	164.6	180	(+9.4)	181	(+10.0)
$C11$ (GPa)	306.2	351	(+14.6)	333	(+8.7)
$C12$ (GPa)	93.8	94	(+0.2)	105	(+11.9)
$C44$ (GPa)	157.0	187	(+19.1)	181	(+15.3)

CS,[13] P86,[14] P91.[15,16] Applications of the correlation-corrected periodic HF methodology to solids[11] include studies of bulk semiconductors,[17] a systematic study of the formation energy of ionic and semi-ionic compounds,[18,2] the interlayer properties and binding energies in MX2 materials,[9,10] and adsorbate-surface binding energies.[19-21]

The Gaussian basis sets used in the present study are described in an earlier work[2] and are expressed here as [Mg/O]. The small basis [8511/8411] resembles a double-zeta set on both the cation and anion and the large basis [8511*/8411*] adds polarization functions to both atoms in the form of a single d shell with the same exponent (a =0.65 bohr^{-1}) on each. The tolerance parameters used to evaluate the Coulomb and exchange series in all of these calculations were ($s_c = t_m = 5$) and ($s_{ex} = p_{ex}^g = 5$ and $p_{ex}^l = 10$).[1] This study extends an earlier investigation of bulk properties of MgO (Ref. 22) and other ionic compounds.[2] The elastic constants reported below are within 5% of those presented by Dovesi *et al.*[2] Errors of this magnitude are likely to result from the use of different schemes for obtaining polynomial fits to the *ab initio* total-energy data. In the present work the elastic constants are described as a function of the magnitude of the fractional displacement vector "distortion parameter" about the equilibrium lattice constant (a =4.205 Å). The reported elastic constants were obtained from polynomial fits of the energetics converged with respect to polynomial order (typically third to fifth order). The phonon frequencies were obtained from quadratic fits of the total energies.

III. RESULTS AND DISCUSSION

A prerequisite to parametrizing any model from *ab initio* data is a quantitative determination of the accuracy of

the *ab initio* method. The present work examines two potential sources of error in the *ab initio* calculations, limitations of the basis set on the calculated properties and the treatment of correlation effects with *a posteriori* correlation corrections to periodic Hartree-Fock theory. The bulk properties of rocksalt MgO examined here are the elastic constants and the (Γ, X, and L) point phonon frequencies.

A. Elastic constants

Table I contains the variation of the calculated lattice spacing and elastic constants as polarization functions are added to the basis set. These data are compared to experimental data measured at T =77 K.[23] The d functions on the cation and anion have little effect on the calculated bulk modulus, but does improve (decrease) $C11$ and $C44$. The change in $C11$ behavior is anticipated as this distortion of the lattice is anisotropic and therefore sensitive to the directional flexibility of the basis set. The computed $C12$ value is correspondingly increased with larger basis because it is intrinsically coupled to B and $C11$ through the relation, $B = 1/3(C11+2C12)$. The inclusion of polarization functions produces a consistent overestimation of the elastic constants by approximately 10%. This is in accordance with previous HF calculations on bulk solid[2] and molecules.[3] The cost of including these functions is a twofold increase in CPU time for a single point energy calculation. Computational requirements precluded a full determination of the basis set limit of the MgO calculations, but an estimate can be made by comparison to a similar study on LiH,[24] an analogous system with fewer electrons per unit cell. The latter work indicated that it was necessary to include p functions on both lithium and hydrogen in order to correctly describe the elastic properties. However, the computed properties varied little with substantial changes (20%) in the exponent of the p orbitals and to the addition of higher angular momentum basis functions (d functions on Li and H). This suggests that the present results will be insensitive to both the optimization of the d exponents and to the addition of f functions.

The data in Tables II and III show the effect of *a posteriori* correlation corrections to the periodic Hartree-Fock calculations for the small and large basis sets, respectively. The computer HF lattice spacing is within +0.5% of the experimental value in both cases. Including correlation corrections causes the lattice parameter to be underestimated by 2.0–2.6%. This decrease in the

TABLE II. Correlation corrected periodic Hartree-Fock calculations of MgO lattice parameter and elastic constants. Experimental values from Anderson, 1966, calculations with [Mg/O] basis [8511/8411].

	Expt.	HF	% error	HF+CS	% error	HF+P86	% error	HF+P91	% error
a (Å)	4.19	4.205	(+0.36)	4.105	(−2.0)	4.101	(−2.1)	4.105	(−2.1)
B (GPa)	164.6	180	(+9.4)	196	(+19.1)	212	(+28.8)	212	(+28.8)
$C11$ (GPa)	306.2	351	(+14.6)	482	(+57.4)	474	(+54.8)	471	(+53.8)
$C12$ (GPa)	93.8	94	(+0.2)	53	(−43.5)	81	(−13.6)	82	(−12.6)
$C44$ (GPa)	157.0	187	(+19.1)	188	(+19.7)	187	(+19.1)	185	(+17.8)

TABLE III. Correlation corrected periodic Hartree-Fock calculations of MgO lattice parameter and elastic constants. Experimental values from Anderson, 1966, calculations with [Mg/O] basis [8511*/8411*].

	Expt.	HF	% error	HF+CS	% error	HF+P86	% error	HF+P91	% error
a (Å)	4.19	4.195	(+0.1)	4.090	(−2.4)	4.079	(−2.6)	4.086	(−2.5)
B (GPa)	164.6	181	(+10.0)	205	(+24.5)	204	(+23.9)	205	(+24.5)
$C11$ (GPa)	306.2	333	(+8.7)	460	(+50.2)	466	(+52.2)	461	(+50.5)
$C12$ (GPa)	93.8	105	(+11.9)	77	(−17.9)	73	(−22.2)	77	(−17.9)
$C44$ (GPa)	157.0	181	(+15.3)	182	(+15.9)	180	(+14.6)	180	(+14.6)

equilibrium lattice constant is directly evident in the computed bulk modulus curves (Figs. 1 and 2). The three correlation functionals are nearly linear increasing functions of the lattice spacing over this range of distortions (see Fig. 2). In polynomial fits to the HF and correlation energies the linear terms are 0.02 and 0.2, respectively. The large positive slope of the functionals produces a correspondingly large negative shift in the equilibrium position ($\delta_{eq}^{HF} = -0.0024$, $\delta_{eq}^{corr} = -0.025$). If the HF bulk modulus cure was quadratic over this region the addition of a linear correlation contribution would have no effect on the second derivative despite changing the lattice spacing (first derivative quantity). The anharmonicity in the HF curves (requiring cubic or higher-order polynomial fits) introduces an explicit dependence on R_{eq} in the computed force constants, hence the bulk modulus is increased by 10–15 % when correlation corrections are included.

Figures 3–6 illustrate analogous effects on the $C11$ and $C44$ curves. The correlation corrected minima for the $C11$ and $C44$ distortions are −0.04 and 0.0, respectively. This produces a large increases (35–40 %) in the $C11$ elastic constant, but no change in $C44$. The greater change in $C11$ with respect to B results in a decrease in $C12$ with the inclusion of correlation. These trends are observed in calculations employing both basis sets; the computed values using the three functionals are, however, more uniform when the larger basis set is used (see Tables II and III).

In Figs. 7 and 8, the HF and correlation contributions to B, $C11$, and $C44$ are compared. Clearly correlation affects B far more than $C11$ or $C44$; this may be understood in terms of a simple model based on variations in nearest-neighbor (NN) and next-nearest-neighbor (NNN) distances. The bulk modulus corresponds to an isotropic distortion of the cubic lattice with 6 NN (Mg-O) and 12 NNN (Mg/Mg or O/O) contacts which increase with increasing lattice parameter. This produces a substantial variation in the computed density along these coordinates and hence a correspondingly large change in the correlation energies. In contrast the $C11$ distortion is anisotropic with two groups of NN and two groups of NNN. Distortions of the lattice (to first order) change 2 NN (Mg-O) distances while fixing the remaining 4 NN; they also alter 8 NNN while 4 NNN are held constant. A crude model of the correlation energy based on the Mg-O distances works rather well—relative changes in B are three times those found in $C11$ for similar changes in δ. The $C44$ distortion does not change the NN distances to first order and hence the effects of correlation are small. These observations indicate that simple pairwise models of the correlation energy may be adequate in this system.

As the correlation energy is being estimated from the local density, which increases as the lattice constant is decreased, it is not surprising that a simple binding term is generated. The elastic constants are strongly affected by the reduction in the lattice parameter produced by this term. In general, correlation increases the size of inert
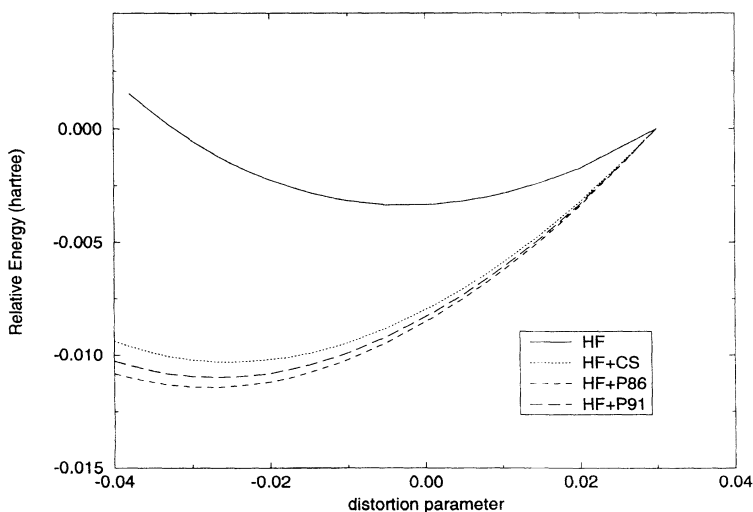

FIG. 1. Bulk modulus. Relative energies as a function of the fractional distortion (d) of the lattice parameter (relative $a = 4.205$ Å). Solid line is HF data and dashed lines include correlation corrections. All curves have been zeroed at $d = 0.03$.
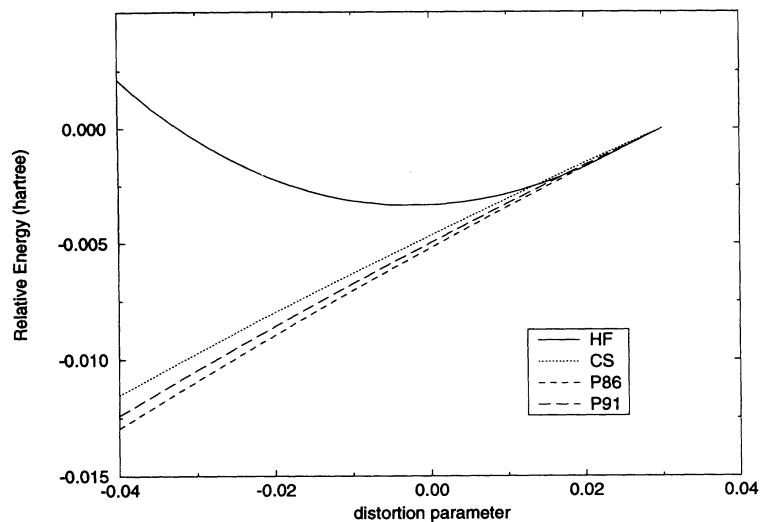
FIG. 2. Bulk models: HF and correlation corrections. Relative energies as a function of the fractional distortion (d) of the lattice parameter (relative to $a = 4.205$ Å). Solid line is HF data and dashed lines are correlation-only values. All curves have been zeroed at $d = 0.03$.

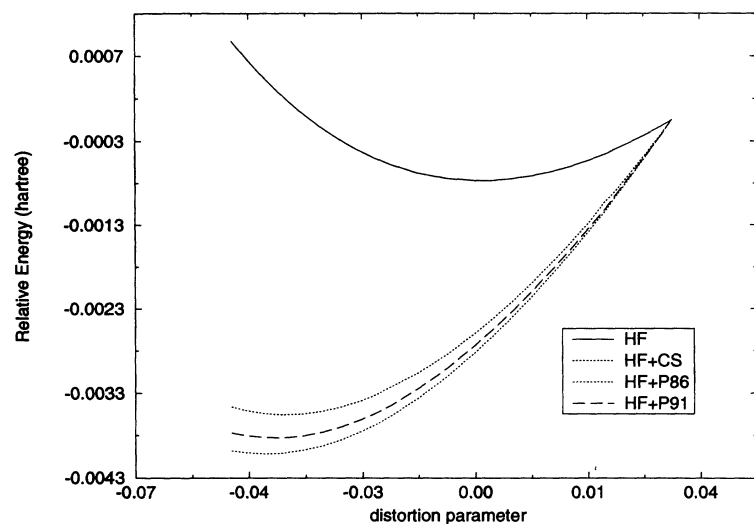FIG. 3. $C11$. Relative energies as a function of the fractional distortion of the lattice corresponding to $C11$ (relative $a = 4.205$ Å). Solid line is HF data and dashed lines include correlation corrections. All curves have been zeroed at $d = 0.02$.
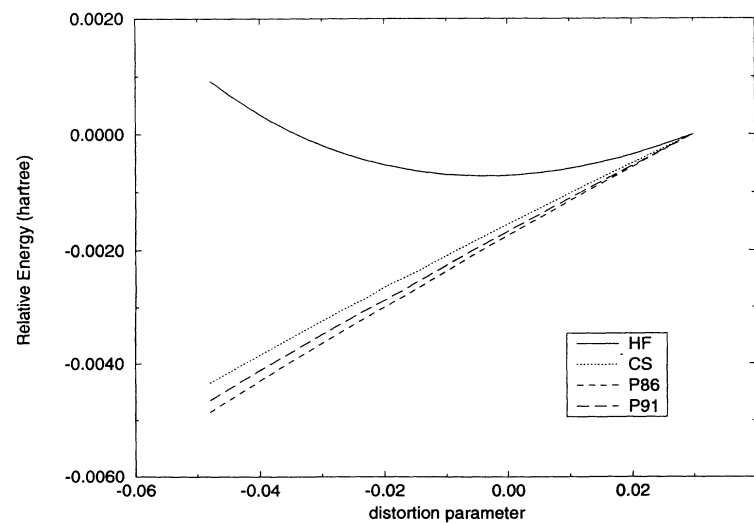

FIG. 4. $C11$: HF and correlation corrections. Relative energies as a function of the fractional distortion of the lattice corresponding to $C11$ (relative $a = 4.205$ Å). Solid line is HF data and dashed lines are correlation-only values. All curves have been zeroed at $d = 0.02$.
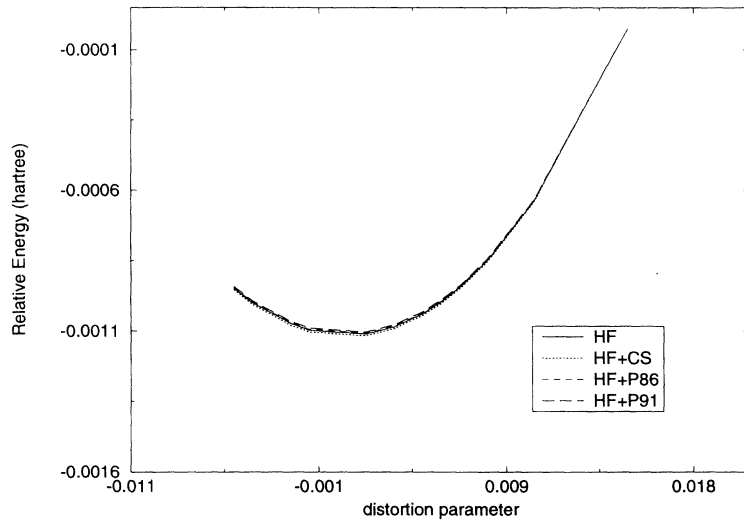
FIG. 5. $C44$. Relative energies as a function of the fractional distortion of the lattice corresponding to $C44$ (relative $a = 4.205$ Å). Solid line is HF data and dashed lines include correlation corrections. All curves have been zeroed at $d = 0.015$.
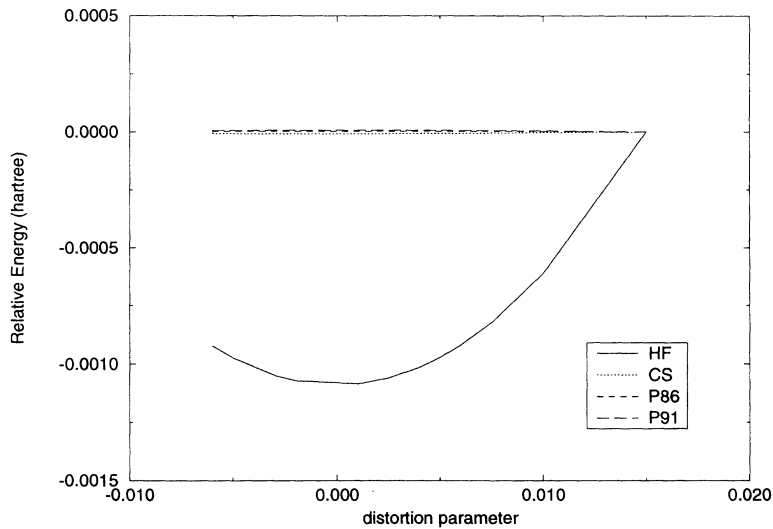

FIG. 6. $C44$: HF and correlation corrections. Relative energies as a function of the fractional distortion of the lattice corresponding to $C44$ (relative $a = 4.205$ Å). Solid line is HF data and dashed lines are correlation-only values. All curves have been zeroed at $d = 0.015$.
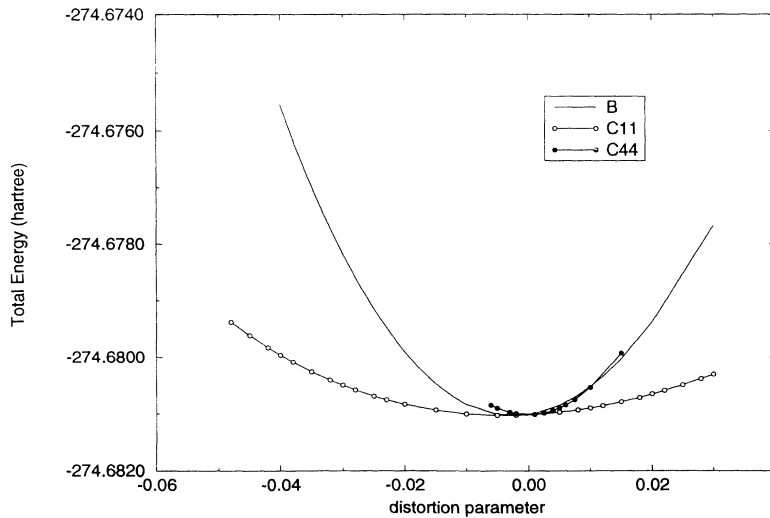

FIG. 7. HF elastic constants. HF total energies for bulk modulus $C11$ and $C44$ as a function of the fractional distortion parameter.
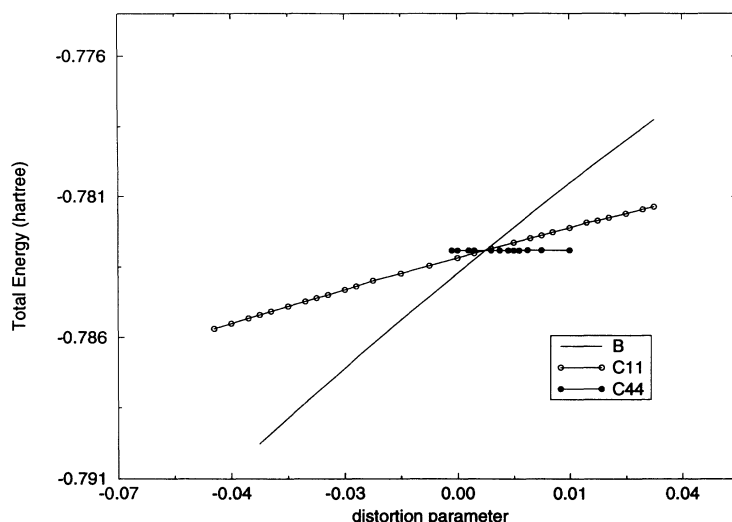
FIG. 8. CS correlation contributions to elastic constants. CS total energies for bulk modulus, $C11$ and $C44$ as a function of the fractional distortion parameter.

gas configurations (such as the oxygen anion). This effect, which is not apparent in the *a posteriori* estimate of correlation, provides a possible mechanism for the correct description of the lattice constant and hence the elastic properties. A discussion of the relative accuracy of different schemes for including *a posteriori* correlation corrections to HF theory is presented in a paper by Causá and Zupan.[25]

B. Phonon frequencies

Phonon frequencies at three special positions in the Brillouin zone (Γ, X, and L) were computed within the frozen-phonon approximation. The X- and L-point phonon motions were generated within tetragonal and rhombohedral unit cells of twice the primitive cell volume. These cells have 16 and 12 symmetry operations and contain two distinct magnesium and oxygen atoms. The supercell matrices used were

$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}$$

and

$$\begin{bmatrix} 1 & 1 & -1 \\ 0 & 0 & 1 \\ 1 & -1 & 0 \end{bmatrix}$$

for the X and L points, respectively.

Phonon eigenvectors were calculated using a dynamical matrix based on an empirically derived dipolar shell model.[26,5] Within this model the oxygen and magnesium sublattice motions are decoupled at the Γ and L points; the optical (acoustic) modes corresponding to the motion of light (heavy) atoms. The displacement vectors corresponding to X-point phonons (computed from the shell model) involve coupled motions of the atomic sublattices. The actual magnitude of this coupling is strongly model dependent; a fully decoupled model was therefore used to generate the *ab initio* X-point energy curves reported below. Although this introduces errors into the computed X-point frequencies, it is in keeping with the original

objective of this study to obtain energy vs distortion data that can be used to parametrize the shell models. The eigenvectors for each mode are shown in Tables IV and V. The symmetry of the system was fully exploited in the calculations. Pairs of like atoms are equivalent in all modes at the X point and in the transverse acoustic (TA) and optic (TO) modes at the L point. The L-point longitudinal optic (LO) displacements produce equivalent oxygens and inequivalent magnesiums and the reverse occurs for the longitudinal acoustic (LA).

At the Γ point the optical modes correspond to relative motion of the Mg and O sublattices. The LO mode produces a dipole moment parallel to k which generates a macroscopic electric field in the crystal. The dipole moment of the TO mode is perpendicular to k thus no macroscopic electric field is created. The Ewald convention used in the *ab initio* calculations precludes the generation of a macroscopic electric field and hence the calculated

TABLE IV. Periodic Hartree-Fock calculations of phonon frequencies using the frozen-phonon approximation. Basis set [Mg/O]. Experimental values from Peckham, 1967.

k point/ mode	Eigenvector/ sublattice	Expt. (THz)	[8511*/8411*] (THz)	% error	[8511/8411] (THz)	% error
Γ						
TA		0.0				
LA		0.0				
TO	$(0dd)$/O	11.8	11.92	$(+1.0)$	13.13	$(+11.3)$
LO		21.7				
X						
TA	$(dd0)$/Mg	8.7	9.99	$(+14.8)$	11.35	$(+30.4)$
LA	$(00d)$/Mg	13.0	14.20	$(+9.2)$	16.93	$(+30.2)$
TO	$(dd0)$/O	13.2	13.70	$(+3.8)$	14.21	$(+7.6)$
LO	$(00d)$/O	16.61	18.76	$(+12.9)$	19.25	$(+15.9)$
L						
TA	$(d0-d)$/Mg	8.8	8.55	(-2.8)	9.24	$(+5.0)$
LA	(ddd)/Mg	16.6	17.68	$(+6.5)$	18.14	$(+9.3)$
TO	$(d0-d)$/O	11.1	11.31	$(+1.9)$	12.01	$(+8.2)$
LO	(ddd)/O	18.5	19.57	$(+5.8)$	19.89	$(+7.5)$

TABLE V. Correlation corrected periodic Hartree-Fock calculations of phonons in MgO. All calculations performed using [Mg/O] basis [8511*/8411*].

k point/ mode	Expt. (THz)	HF (THz)	HF % error	HF+CS (THz)	HF+CS % error	HF+P86 (THz)	HF+P86 % error	HF+P91 (THz)	HF+P91 % error
Γ									
TA	0.0								
LA	0.0								
TO	11.8	11.92	(+1.0)	11.31	(−4.1)	11.46	(−2.9)	11.46	(−2.9)
LO	21.7								
X									
TA	8.7	9.99	(+14.8)	9.72	(+11.7)	9.84	(+13.1)	9.85	(+13.2)
LA	13.0	14.20	(+9.2)	13.75	(+5.8)	13.92	(+7.1)	13.93	(+7.1)
TO	13.2	13.70	(+3.8)	11.91	(−9.8)	11.98	(−9.2)	12.00	(−9.1)
LO	16.61	18.76	(+12.9)	18.18	(+9.4)	18.27	(+10.0)	18.28	(+10.0)
L									
TA	8.8	8.55	(−2.8)	8.20	(−6.8)	8.28	(−5.9)	8.29	(−5.8)
LA	16.6	17.68	(+6.5)	17.45	(+5.1)	17.45	(+5.1)	17.47	(+5.2)
TO	11.1	11.31	(+1.9)	10.88	(−2.0)	10.92	(−1.6)	10.94	(−1.4)
LO	18.5	19.57	(+5.8)	19.14	(+3.4)	18.99	(+2.6)	19.01	(+2.8)

frequency corresponds to the transverse optical mode at the Γ point.

In Table IV the basis set dependence of the phonon frequencies is reported along with the corresponding experimental data.[7,27,28] In accordance with molecular HF calculations, periodic HF theory tends to overestimate vibrational frequencies.[3] The presence of polarization functions reduces the phonon frequencies and improves the agreement with experiment. This effect is largest for the X-point TA and LA modes. At the X point the longitudinal and transverse modes produce large changes in the Mg-O distances and hence large anisotropic (tetragonal) distortions of the local charge density. At the L point longitudinal modes correspond to atoms moving into the interstices of neighboring layers and the transverse modes move planes of like atoms past each other. The L-point modes all produce a more isotropic (rhombohedral) distortion of the local charge density. One might therefore expect that greater angular flexibility in the local basis functions would better describe the X-point modes. This prediction could not be tested because

the inclusion of local functions with f symmetry has not been implemented into the CRYSTAL package. However, analogous studies of LiH indicated that the basis set should be converged when d functions are present.[24] As noted above the X-point frequencies are also in error due to the approximate nature of the eigenvectors used. Calculations of the Γ-point TO frequency when the d functions were removed from either the cation or anion indicated that both sets were necessary to properly describe the vibration (d function on Mg only, 12.33 THz; O only, 12.58 THz).

An additional factor that could affect the computed vibrational constants is nonzero coupling between the motions of light and heavy atoms. The shell-model calculations predict a small coupling between the LA and LO modes (and correspondingly between the TA and TO modes) at the X point. The absolute magnitude of this coupling is inherently model dependent and therefore has not been explicitly treated in the present frozen-phonon construction. A more accurate description of these modes would be expected to reduce the acoustic and in-
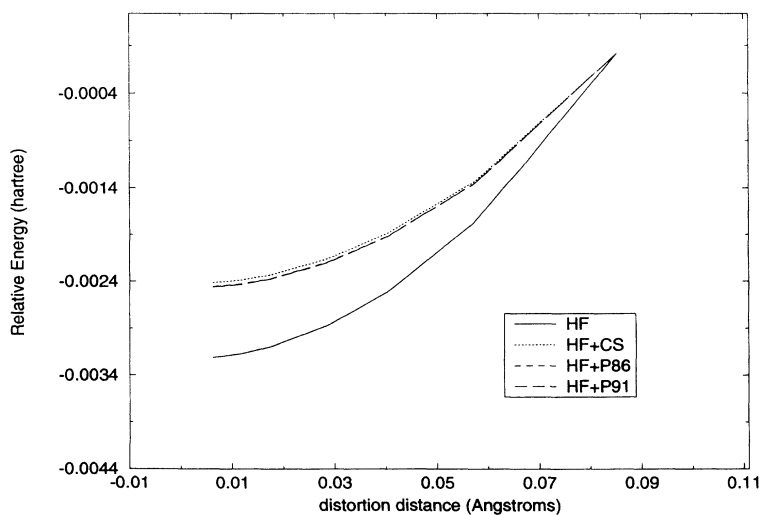

FIG. 9. X-point TO mode. Relative HF (solid line) and correlation corrected (dashed lines) energies as a function of distortion distance from equilibrium ($a = 4.205$ Å).
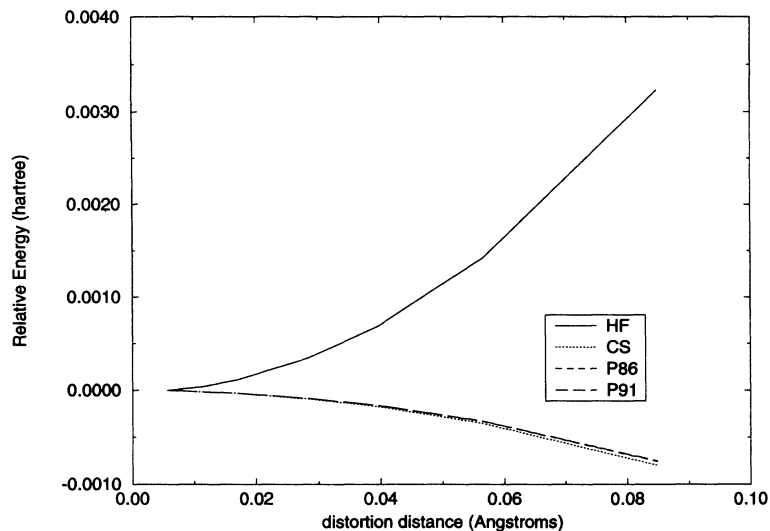
FIG. 10. X-point TO mode: HF and correlation corrections. Relative HF (solid line) and correlation-only (dashed lines) energies as a function of distortion distance from equilibrium ($a = 4.205$ Å).

crease the optic frequencies, thus further reducing the theoretical-experimental error.

The correlation corrected phonon frequencies are reported in Table V and the X-point TO curves are shown in Figs. 9 and 10 (only the larger and more accurate basis set was used) and the lattice constant was fixed at 4.205 Å. The *a posteriori* treatment of correlation softens all of the lattice vibrations, consistent with the results found for correlation corrected vibrational frequencies in molecules.[3] The frequency of the Γ-point TO mode was recalculated using the correlation corrected optimized lattice parameter (4.09 Å) and the resulting values were 14.39, 13.92, 13.82, 13.80 THz for HF, HF+CS, HF+P86, and HF+P91, respectively. As observed in calculating the elastic properties the reduction of the lattice constant by 2% increases the curvature of the energy surfaces (due to the anharmonicity of the underlying HF energy surface) and thus the phonon frequencies by approximately 20%. At a given lattice constant the correlation correction softens the modes relative to HF. One expects this effect because as an atom moves away from its equilibrium position the density overlaps increase resulting in a rise in the correlation energy. The resultant attractive potential softens the HF repulsive term. The magnitudes of the correlation corrections (typically $<5\%$) in the phonon calculations are substantially less than those computed for the elastic constants. This is not unexpected since the elastic constant distortions change the cell volume and therefore greatly perturb the charge density of the lattice. Atomic displacements in a lattice vibration (at a fixed volume) will have much less of an effect on the electron density distribution.

IV. CONCLUSIONS

Ab initio periodic HF and correlation corrected periodic HF theory was used to calculate the bulk properties of MgO. The inclusion of polarization functions in the basis sets on both the cation and anion resulted in a slightly improved lattice constant and errors in the elastic constants consistent with previous studies of ionic compounds indicating that the calculations were close to the HF limit. The computed HF lattice parameter is in very good agreement with experiment (% error $<0.5\%$) and the elastic constants are overestimated; the computed values are within 15% of the empirical data (values extrapolated to $T=0$ K). *A posteriori* correlation corrections to the HF energies reduce the lattice parameter (% error -2.0%) and hence further stiffen the elastic constants (worsening the theoretical-experimental error). The anisotropic $C11$ distortion was particularly sensitive to the inclusion of correlation corrections. Phonon frequencies were computed within the frozen-phonon approximation at the (Γ, X, and L) points in the Brillouin zone. The HF values were in good agreement with experiment (errors -3 to $+15\%$). The X-point TA and LA modes were especially sensitive to the inclusion of polarization functions in the basis set. Correlation corrections reduced all the vibrational frequencies by 3–5 % and improved the agreement with experiment. The parametrization of electrostatic shell models from these data will be presented in a future work.

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