

ER-BOC Calculations of Crystal Bulk Properties from Smallest-Cluster Models

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Abstract: Ab initio calculation of bulk properties of crystals with a high accuracy, which is a long-time goal of solid chemistry and physics, is still difficult and expensive because a large cluster is required as a crystal structure model. This article proposes a model based on density functional theory (DFT) quantum chemistry calculations and the assumption that the bond order of a given atom with its nearest atoms in a compound is conserved over the entire range from its diatomic molecules to clusters and further to crystals. This entire range bond order conservation (ER-BOC) provides an effective way to correlate bulk properties of crystals with those of the corresponding molecules and small clusters. By combining this ER-BOC principle with hybrid DFT quantum chemistry calculations, accurate predictions of the bulk bond lengths of a crystal can be made using calculations on small clusters.

1. Introduction

Bulk properties, such as bond lengths, which can be used to calculate the lattice parameters of solid crystals, are very useful information in solid state chemistry and physics, catalysis, surface science, and material science. Ab initio quantum chemistry calculations have made great progress in those fields. However, accurate calculations of bulk bond lengths are still difficult. This happens because current quantum calculations are based on small clusters consisting of only a few atoms. The small-cluster structures are different from that of the respective bulk solid due to truncation effects. To minimize this effect, a large cluster is needed as a computational model. However, applications of all-electron molecular orbital calculations are often restricted to small systems because the computational time increases rapidly with the number of atoms. In this article, we report a conservation principle that holds for various sizes of a compound, ranging from diatomic molecules to clusters and bulk crystals. On the basis of this conservation principle, accurate predictions of bulk bond distances may be based on calculations on small-cluster models consisting of several atoms.

2. Theoretical Model and Calculation

The bond length depends on the bond strength, which depends on bond order. Pauling proposed a correlation between bond order and equilibrium bond length:¹⁻³

$$x = \exp[-(r - r_e)/a] \quad (1)$$

He defined the bond order (x) as the number of shared electron pairs. The parameters r_e and a are the equilibrium bond length of a A–B single bond ($x = 1$) and an empirical parameter, respectively. This correlation has found fruitful applications in chemical kinetics and in examination of transition state structures.⁴⁻⁷ For various linear three-center A···B···C interactions, the conservation of the Pauling bond order, in terms of which the sum of the bond orders of the making and breaking bonds along the minimum-energy path is constant and is equal to unity, was already assumed^{8,9} and shown to be accurate, both computationally¹⁰⁻¹² and experimentally.¹³ This bond order conservation principle serves as a basis for the familiar BEBO (bond energy–bond order) method.^{14,15} In addition, another principle of bond order conservation for adsorbed species, in which total bond order for interactions between an adsorbed atom and solid surface is conserved, was also assumed for calculations of adsorption energies.^{16,17} However, a critical issue related to the bond order is whether the total bond order between

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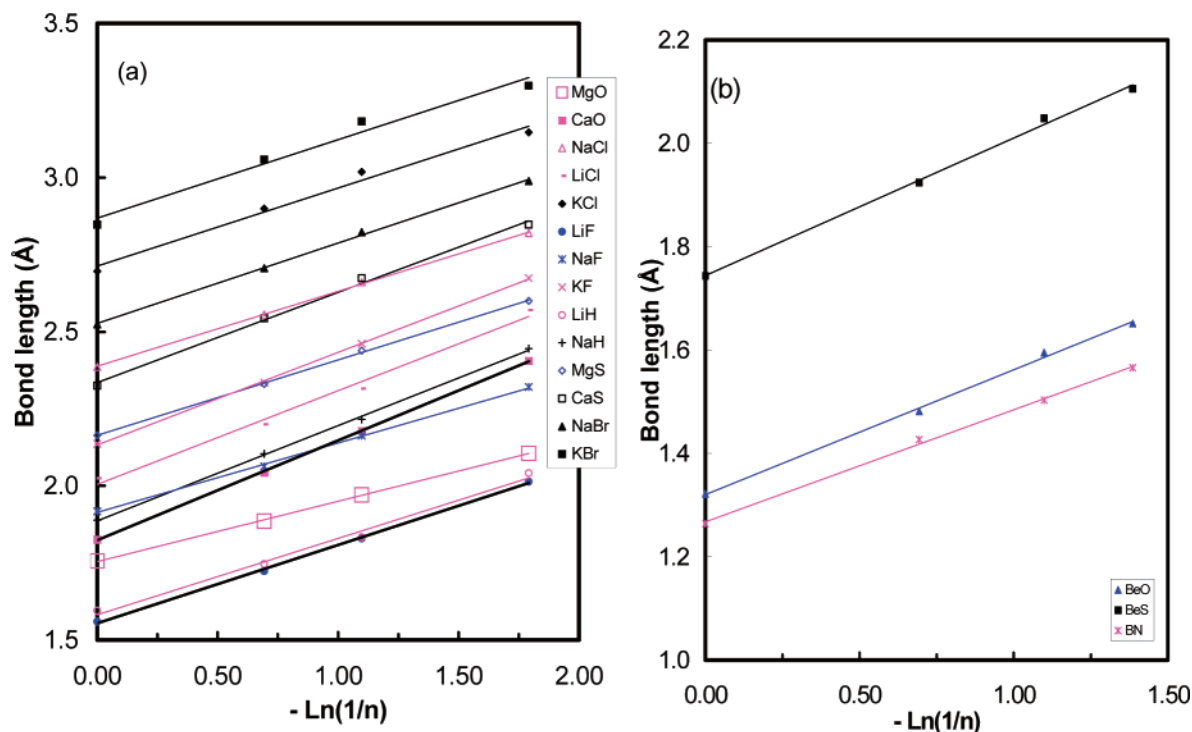


Figure 1. Bond length vs $\ln(1/n)$: (a) rock-salt structure compounds and (b) non-rock-salt structure compounds.

a given atom and all its nearest atoms in a compound is the same in molecules, clusters, and crystals, i.e., whether the total bond order for a given atom of a compound is conserved over the entire range. In what follows, various **AB**-type compounds, i.e., binary compounds with 1:1 stoichiometry, were selected to evaluate this issue because the most popular ionic compounds belong to this type.

For **AB**-type compounds, total bond order (x) for a given atom of a compound, whether in a molecule, cluster, or solid crystal, can be expressed as follows:

$$x = \sum_{i=1}^n x_i \quad (2)$$

where n is the coordination number of the given atom and x_i is the bond order of the given atom with the i th nearest atom. Because each bond of **A** with all its nearest **B** is the same in a stable structure, i.e., $x_1 = x_2 \dots = x_n$, and if the total bond order of each atom is assumed to be conserved and normalized to unity, then

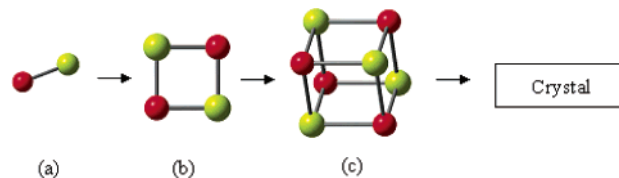
$$x_1 = x_2 \dots = x_n = 1/n \quad (3)$$

Combining eqs 1 and 3 yields

$$r = r_c - a \ln(1/n) \quad (4)$$

Therefore, if there is a linear relationship between the bond length and $\ln(1/n)$, the bond order conservation is valid. A given atom has a different coordination number (n) in molecules, clusters, and the bulk crystal. If eq 4 can relate these various bond lengths to the corresponding coordination numbers, the total bond order is conserved in the entire range of compound sizes.

A popular hybrid density functional theory (DFT) method, the B3LYP with the 6-311G* basis set,¹⁸ which is a combination of the Hartree–Fock theory and Becke’s three-parameter exchange with the Lee–Yang–Parr (LYP) correlation potential,^{19,20} was used to optimize the structures of the following three models (representing a diatomic molecule and two clusters) with coordination numbers of 1, 2, and 3, respectively. All calculations were carried out using the Gaussian 98 package.²¹



We used eq 4 to correlate the bond lengths of the diatomic molecule (model a), four-atom cluster (model b), and eight-atom cluster (model c) obtained by the hybrid DFT calculations in this work and bulk bond lengths of crystals obtained by experiments from ref 22 with their coordination numbers. As

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shown in Figure 1, the bond lengths in a molecule, two clusters, and the bulk crystal provide a linear relationship with their coordination numbers for each of the 17 popular compounds considered. This demonstrates that the total bond order is constant over the entire range of compound sizes, which will be called entire range bond order conservation (ER-BOC). However, it is worthwhile to note that the bond lengths calculated for a nonstoichiometric cluster (B–A–B) have a large deviation from the conservation line (see Supporting Information). This indicates that the stoichiometry principle plays an important role in the ER-BOC.

Based on the entire range bond order conservation (eq 4), the bond length (r_{sc}) of the smallest stoichiometric AB-type cluster with a coordination number of 2, which consists of just four atoms, can be related to its coordination number as follows:

$$r_{sc} = r_e - a \ln(1/2) \quad (5)$$

Substituting eq 5 into eq 4 yields

$$r = r_e + (r_{sc} - r_e) \frac{\ln(n)}{\ln(2)} \quad (6)$$

One can obtain r_e and r_{sc} from quantum calculations based on a diatomic molecule and a four-atom cluster (models a and b) and then calculate the bulk bond length of a solid crystal using eq 6 without any empirical parameters. Using this method, 18 crystals, including wurtzite, zinc blende, and rock salt structure crystals, were calculated, and results are listed in Table 1. One can see that all calculated bond lengths are very consistent with the experimental values, with most of absolute errors below 0.05 Å or even below 0.001 Å.

To compare the above calculation with those based on the conventional hybrid DFT methods, the MgO was selected as an example. As reported,²³ even when a large MgO cluster containing 64 atoms ($4 \times 4 \times 4$) was used, the Mg–O bond length provided by the conventional hybrid DFT calculation was 2.02 Å, which differs from the experimental bulk bond length of 2.105 Å by 0.075 Å. In contrast, the bulk Mg–O length calculated using the present method is 2.091 Å, which differs by 0.014 Å from the experimental value. This new method not only yields more accurate results but also requires several thousand times less computational effort than the conventional large-cluster hybrid DFT calculation. In the DFT quantum chemistry ER-BOC calculation, all-electron molecular orbital calculations are needed only for the diatomic molecule and a four-atom cluster.

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Table 1. Solid Crystal Bulk Bond Lengths

compd	crystal	n^a	r_e^b (Å)	r_{sc}^b (Å)	r_{bulk}^c (Å)	r_{exp}^d (Å)	error $r_{bulk} - r_{exp}$ (Å)
BeO	wurtzite	4	1.3214	1.4817	1.6420	1.6512	0.0092
BeS	zinc blende	4	1.7432	1.9243	2.1054	2.1054	0.0000
MgO	rock salt	6	1.7564	1.8857	2.0906	2.1056	0.0150
MgS	rock salt	6	2.1633	2.3304	2.5952	2.6000	0.0048
CaO	rock salt	6	1.8262	2.0434	2.3877	2.4053	0.0176
CaS	rock salt	6	2.3255	2.5432	2.8882	2.8474	0.0408
BN	zinc blende	4	1.2637	1.4268	1.5899	1.5657	0.0242
LiF	rock salt	6	1.5598	1.7229	1.9814	2.0135	0.0321
LiCl	rock salt	6	2.0244	2.1988	2.4752	2.5698	0.0946
LiBr	rock salt	6	2.1769	2.3617	2.6546	2.7507	0.0961
LiH	rock salt	6	1.5948	1.7462	1.9862	2.0415	0.0553
NaF	rock salt	6	1.9178	2.0635	2.2944	2.3200	0.0256
NaCl	rock salt	6	2.3857	2.5553	2.8241	2.8201	0.0040
NaBr	rock salt	6	2.5237	2.7062	2.9955	2.9886	0.0069
NaH	rock salt	6	1.8887	2.1042	2.4458	2.4450	0.0008
KF	rock salt	6	2.1363	2.3354	2.6510	2.6735	0.0225
KCl	rock salt	6	2.696	2.8992	3.2213	3.1466	0.0747
KBr	rock salt	6	2.8474	3.0581	3.3921	3.2983	0.0938

^a Coordination number. ^b Parameters obtained for eq 6 from DFT calculations. ^c Bulk bond lengths calculated in this work. ^d Experimental bulk bond lengths from ref 22.

Nevertheless, it is worthwhile to note that this ER-BOC model seems not to be suitable for some compounds with strong covalent character. For example, C₆₀, in which all the carbons have the same coordination number, has two kinds of C–C bond lengths. In addition, for some semiconductor compounds such as GaAs, the ER-BOC model is still applicable, but with a relative high error (about 8%) in the prediction of the bond lengths.

3. Conclusion

In conclusion, an entire range bond order conservation principle was suggested. On the basis of this conservation principle, accurate predictions of the bulk bond lengths of solid crystals were obtained using a negligible computational time even with a regular PC computer.

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Supporting Information Available: Figures regarding comparison between stoichiometric and nonstoichiometric clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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