On the Accuracy of the Total Energy Pseudopotential Scheme Applied to Small Molecules

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The accuracy of the calculation of the equilibrium geometry of small molecules using the pseudopotential solid state code CASTEP is analyzed. The results of the density functional calculations are presented for alkaline earth dihalides and for the metal−organic molecule $Ba(C_5H_5)_2$. The density functional theory predicts qualitatively correct geometry in all cases where the accuracy of 0.01 eV in total energy is sufficient to distinguish between different local extrema. CASTEP implementation of the gradient-corrected exchange-correlation functional is shown to be in all cases superior to the local density approximation approach.

Introduction

We report the results of the systematic test of the solid state pseudopotential total energy method[1] applied to the family of molecules that are of fundamental interest for organometallic chemistry. We calculated the equilibrium geometry of 20 triatomic molecules of the MX_2 composition, where M = Be, Mg, Ca, Sr, Ba and X = F, Cl, Br, I. Further, the same technique was applied to the Cp_2Ba molecule, a prototype organometallic compound which has a cyclopentadienyl group substituted for both halogen atoms. The density functional theory (DFT) was used either in local density approximation (LDA)[2] or in the generalized gradient approximation (GGA),[3] and the results obtained using these two methods were compared to the available experimental data.

Recent interest in these molecules is in the quest for an explanation of their anomalous shape.[4−12] The dihalides of light alkaline earth elements are all linear, while some of the heavier members of this family are bent with a bond angle in the range from 100 to 155°. The energy difference between bent and linear configurations of these triatomic molecules is known to be rather small, of the order of 0.04−0.12 eV per molecule,[6] presenting a stringent test for any theoretical method. The bent geometry was also observed for a number of Cp_2M compounds, where Cp refers to the cyclopentadienyl ring C_5H_5, the pentamethylcyclopentadienyl ligand C_5Me_5, or even more complex cyclopentadienyl-based ligands.[11,12] Such metallocenes are of substantial interest in chemistry of catalysis, which explains a number of recent experimental and theoretical studies of these and related systems. The aim of the present paper is to demonstrate the applicability of the density functional theory in pseudopotential plane-wave formulation to this kind of problem.

Further motivation for this study comes from the growing interest in applications of the pseudopotential total energy method to the study of interactions between molecules and solids, including energetics of transition structures. Recent examples include investigations of chemisorption,[13,14] surface adsorption and diffusion,[15] chemical decomposition,[16] physisorption,[17] hydration of minerals,[18] etc. These applications require an accurate quantum mechanical description of a bulk solid (or of its surface) with and without a molecule and also of an isolated molecule, using the same computational tool. Accurate quantum chemisry methods cannot be used for periodic systems with a few hundred atoms per supercell,[15,16] leaving the solid state DFT technique as the only alternative in many cases. Pseudopotential plane-wave-based codes (e.g., CASTEP[1]) are known to provide an accurate description of the properties of solids and surfaces;[13−18] however, much less information is available on their applicability to the study of isolated molecules. The results reported below increase one's confidence in using the solid state technique to obtain molecular properties required to study solid−molecule interactions.

Pseudopotential Total Energy Method

The technique used here[1] is based on the efficient minimization of the total energy of the many-electron periodic system within the DFT formalism. Periodic boundary conditions are imposed via the use of supercells; i.e., the molecule under study is placed in a box that has to be sufficiently large to eliminate interactions between periodic images. We chose to use cubic cells with the cell edge of 7 Å for the alkaline earth dihalides and of 10 Å for the Cp_2Ba molecule, with the alkaline earth atom always placed in the cell center.

The imposed periodicity allows one to utilize the Bloch theorem and to use the plane-wave basis set to expand single-electron wave functions. The total energy functional is then minimized in the space of expansion coefficients using the conjugate gradient iterative technique.[1] The minimizer is capable of simultaneous updating of all wave functions,[19] which turns out to be at least two times faster than the original band-by-band minimization algorithm.[20]

Exchange-correlation effects in the electron gas are taken into account either within LDA using Perdew−Zunger parametrization of Ceperley−Alder results[2] or within GGA in the Perdew−Wang formulation.[3] It is difficult to underestimate the importance of using the gradient-corrected functional in the studies of solid−molecule interactions. It has been shown that the GGA results for, e.g., the chemisorption energy of CO on the Pd surface[13] or the dissociation path of H_2 on metallic surfaces[17] are in much better qualitative and quantitative agreement with experiment than are the LDA data. The GGA implementation in CASTEP by White and Bird[21] is no more expensive computationally than the LDA version, and the gradient-corrected functional is used throughout the calculation rather than as a post-SCF perturbative correction.

TABLE 1: Pseudopotential Optimization Parameters: the Choice of Local and Nonlocal Projectors, the Values of the Core Radii r_c, and the Kinetic Energy Minimization Filters Q for Different Orbital Momenta

element	local component	nonlocal components	r_c (s) (Bohr)	r_c (p) (Bohr)	r_c (d) (Bohr)	Q (s)	Q (p)	Q (d)
F	p	s	1.6	1.5	1.6	1.15	1.15	1.1
Cl	p	s, d	1.7	1.7	1.7	1.0	1.0	1.0
Br	0.7p + 0.3d	s	1.89	1.89	1.89	1.0	1.0	0.9
I	p	s, d	2.3	2.3	2.3	1.0	1.0	1.0
Be	s	p	1.4	1.4		1.0	1.0	
Mg	s		2.0			1.0		
Ca	p	s	2.0	2.0		0.9	1.06	
Sr	p	s	1.6	1.6		0.7	0.7	
Ba	p	s, d	2.7	2.7	2.7	0.4	0.8	0.5

One k-point (Γ point) was used for the Brillouin zone sampling, since supercells were large enough to eliminate dispersion of electronic states. The energy cutoff for the plane waves was 300 eV for all alkaline earth dihalides except for the fluorides where a 700 eV cutoff was chosen. These values guarantee that the total energy convergence with respect to the basis set size is better than 0.01 eV per molecule. The study of the Cp_2Ba molecule was carried out with a 500 eV cutoff energy, which was sufficient for the convergence of energy differences and of structural parameters, although this value does not correspond to the absolute convergence of the total energy.

The norm-conserving pseudopotentials generated using the Kerker scheme[22] were used in the Kleinman−Bylander representation.[23] The pseudopotentials were optimized when necessary to achieve good convergence with respect to the basis set cutoff energy.[24] The optimization strategy is based on the fact that the total energy convergence is largely determined by the convergence rate of the kinetic energy, and the latter is the same for atomic pseudo-wave functions and for valence wave functions in solids or molecules. The optimization scheme suggested in ref 24 uses a small number of Bessel functions, $j_l(q_ir)$, to express the pseudo-wave function inside a core radius r_c. The corresponding wave vectors q_i are found from the requirement of matching of the logarithmic derivative of the pseudo-wave function with that of the all-electron wave function at r_c. The coefficients in the Bessel functions expansion are determined by the following constraints: normalization of the wave function, continuity of the first derivative at r_c, and minimization of the kinetic energy of components with wave vectors higher than a certain cutoff vector q_c.

We use the three-term Bessel function expansion scheme which is a further development over the four-term method.[24] In this formulation the constraint of continuity of the second derivative of the wave function at r_c is removed; thus, the pseudopotential is allowed to have a kink in real space. The kink amplitude and the convergence of the kinetic energy are further controlled in this scheme by selecting the best cutoff vector q_c. The usual choice is to set $q_c = q_3$, where q_3 is the highest wave vector of the Bessel function expansion. We found that in many cases the choice of $q_c = Qq_3$, where Q is not equal to 1, gives more freedom in optimization and results in softer potentials. Thus, the optimized potential is specified by the starting electronic configuration, the values of r_c and Q for each nonlocal projector, and the choice of the local component. We found that in many cases it is possible to select the values of Q in such a way that some pseudopotential components become similar and their average can be used as a local potential, thus reducing the number of nonlocal projectors. This projector reduction technique can speed up the calculations significantly if it results in elimination of, e.g., p and d components, the most computationally intensive ones.

The details of the pseudopotentials used are given in Table 1. All s and p projectors for halogens were computed using

TABLE 2: Equilibrium Bond Lengths (in Å) of the Diatomic Halogens Calculated using LDA or GGA Approximations for the Exchange-Correlation Potentials

molecule	LDA	GGA	expt[4]
F_2	1.39	1.40	1.42
Cl_2	1.97	1.97	1.99
Br_2	2.25	2.26	2.28
I_2	2.65	2.65	2.67

the reference electronic configuration s^2p^5, while the d component was constructed from the doubly ionized configuration $s^1p^{3.75}d^{0.25}$. We neglected the d projector contribution for fluorine since the corresponding part was small and its relevance is questionable (the d projector was constructed from a highly excited state with an occupied 3d level). In fact, the use of this projector resulted in systematically underestimated molecular bond lengths by 0.02−0.03 Å as compared to the results obtained with the s-only nonlocal potential. In case of bromine we succeeded in applying the projector reduction strategy, which resulted in the accurate s-only nonlocal potential.

Potentials for light alkaline earth metals were constructed from neutral configurations, namely s^1p^1 for Be and s^2 for Mg. The resultant purely local potential for Mg is surprisingly accurate and transferable. For example, the calculation of the lattice properties of magnesium oxide performed at the GGA theory level produces the lattice constant of 4.21 Å (experimental value is 4.19 Å) and the bulk modulus of 182 GPa (experimental value is 167 GPa). Unfortunately, in all other cases studied here we found it was impossible to construct purely local pseudopotentials.

Potentials for heavy alkaline earth elements were generated from doubly ionized configurations, s^2p^6 for Ca and Sr and $s^2p^{5.75}d^{0.25}$ for Ba. Further, the barium atom was treated using a fully relativistic approach. The charged configurations used for these elements guarantee good transferability of pseudopotentials and eliminate the need for nonlinear core correction since we treat outer core electrons as valence. We find that it is necessary to include the d projector for Ba since the s-only nonlocal potential gives bond lengths for barium dihalides that are too short by as much as 0.07 Å when compared to the results obtained with the sd nonlocal potential.

As part of the test of pseudopotentials, we calculated the equilibrium bond lengths of diatomic halogens (see Table 2). The bond lengths obtained with LDA are systematically underestimated by 1−2% as a result of the well-known overbinding effect. The LDA error is slightly reduced when we use the GGA functional. The achieved 1% accuracy of the theoretical bond lengths is acceptable from the point of view of studies of solid−molecule interactions, since the accuracy of the DFT calculations of lattice constants of solids is of the same order of magnitude.

Total Energy Pseudopotential Scheme

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Results and Discussion

The structure of the alkaline earth dihalides has been a subject of numerous theoretical[5,6] and experimental[7−11] studies. These molecules represent an attractive test suite for new theoretical approaches. The challenge is to reproduce correctly the anomalous shape of the triatomic molecules in this family. All beryllium and magnesium dihalides are known to be linear, while a bent structure is favored for some molecules where the radius of the metal ion is large compared to the size of the halogen atom. There exists extensive experimental information on the bond lengths in these molecules;[7−11] thus, the theory that would provide both the right shape and the right bond length can be considered to be qualitatively and quantitatively correct for this class of objects.

The most popular theoretical explanations of the observed trends in the structure of dihalides are based on semiempirical arguments. For example, the polarizability of the alkaline earth elements increases down the group, and this might be used as the key feature that explains the bent structures of the dihalides of heavier elements. An extensive review of such polarized-ion models of chemical bonding in this system can be found in, e.g., refs 6 and 11. The most plausible explanation of the molecular shape is that the $(n-1)$d orbitals of the metal atom are more important to the bonding than are the np orbitals. In other words, the observed shapes reflect the competition between sd (bent) and sp (linear) hybridization. This argument is strongly supported by the analysis of the changes in Mulliken populations as a function of the bond angle.[6] However, multiple attempts to calculate the properties of some of the key triatomic molecules like CaF_2 demonstrated that the accuracy of the modern quantum-chemical methods is often insufficient to reproduce experimentally observed geometry—depending on the basis set size and on the details of calculation, either a bent or a linear shape might be predicted (see ref 6 for an authoritative review).

Our calculations were organized as follows. For each molecule we found the total energy and equilibrium bond length in the linear conformation. The search for the global minimum was performed by allowing for a bent molecular geometry. If a stable bent configuration was found, then the preference for either a linear or a bent shape was deduced from the comparison of the total energies. The calculated bond lengths and bond angles in equilibrium geometries are presented in Table 3 where they are compared to available experimental data. It should be noted that the measured bond lengths obtained from room temperature gas-phase experiments are expected to be slightly higher than the theoretical values which refer to 0 K. Further, the data available for a number of molecules (SrF_2, BaF_2, $BaBr_2$) leave the question of their shape open in view of contradictory experimental evidences.[8] With this in mind, the agreement between the GGA results and the experimental data is satisfactory. The typical error in bond length is 1−1.5%, while LDA produces higher discrepancies of the order of 2−3%. It is worth noting that the GGA results are never in worse agreement than are the LDA ones. The gradient corrections systematically decrease the overbinding error when it is present in LDA (e.g., BaF_2, $SrCl_2$, etc.), but they do not destroy agreement with experiment in those cases where LDA is accurate enough (e.g., $MgCl_2$, $CaBr_2$).

There is only one case of SrI_2 where both LDA and GGA predict a bent geometry for the molecule that is known to be linear. However, the calculated energy difference between the two configurations is only 0.04 eV in LDA and a mere 0.01 eV in GGA. The conclusion in this case is that the potential energy surface is so shallow that the accuracy required is too

TABLE 3: Equilibrium Bond Angles and Bond Lengths Calculated using LDA or GGA Approximations for the Exchange-Correlation Potentials

molecule	bond angle (deg)			bond length (Å)		
	LDA	GGA	expt	LDA	GGA	expt
BeF_2	180	180	180[7]	1.43	1.44	
MgF_2	180	180	180[7]	1.77	1.76	1.77[6]
CaF_2	162	147	140−155[7] 140−145[8] 142[9]	2.04	2.07	2.10[7]
SrF_2	158	149	108, 135[6] 108, 180[7]	2.10	2.13	2.20[7]
BaF_2	155	139	100, 115[6] 100, 180[7]	2.21	2.28	2.32[7]
$BeCl_2$	180	180	180[6]	1.80	1.79	
$MgCl_2$	180	180	180[6]	2.18	2.17	2.19[6] 2.13−2.19[7]
$CaCl_2$	180	180	180[6]	2.49	2.51	2.48[6] 2.45−2.51[7]
$SrCl_2$	129	133	120, 142[6] 120[8] 130[10]	2.55	2.58	2.62−2.67[8]
$BaCl_2$	114	113	100, 127[6] 120[10]	2.67	2.70	2.77−2.82[6]
$BeBr_2$	180	180	180[7]	1.93	1.92	
$MgBr_2$	180	180	180[7]	2.31	2.30	2.34[8]
$CaBr_2$	180	180	180[7]	2.64	2.66	2.62−2.67[8]
$SrBr_2$	180	180	180[7]	2.78	2.77	2.82[8]
$BaBr_2$	116	118	180; bent[7] 150[8]	2.82	2.86	2.99[8]
BeI_2	180	180	180[7]	2.15	2.15	
MgI_2	180	180	180[7]	2.53	2.53	2.54[10] 2.52[11]
CaI_2	180	180	180[7]	2.87	2.88	2.83[7] 2.76−2.88[8]
SrI_2	134	154	180[7]	2.93	2.98	3.01−3.03[7]
BaI_2	116	115	148[7]	3.06	3.10	3.15−3.20[7]
Cp_2Ba	134	144	148[11]			

high for the technique we used. The accuracy higher than 0.01 eV/molecule is practically never necessary in solid state applications. Moreover, this energy difference is small compared to the thermal energy, which implies that the molecule in question has no stable geometry even at room temperature.

Alkaline earth dihalides represent the simplest examples of anomalously bent molecules with a central metal atom. Another well-known case of bending that is attributed to hybridization on the central atom can be found among organometallic molecules X_2M, where X is either a cyclopentadienyl C_5H_5 or a pentamethylcyclopentadienyl C_5Me_5, and M is either Ca, Sr, or Ba (Be and Mg compounds are linear). There is a certain controversy as to the driving force for bending, with the alternative explanations being either sd hybridization[11] or van der Waals interaction between the ligands.[12] The bending angle of the $M(C_5H_5)_2$ and $M(C_5Me_5)_2$ molecules is usually the same within 2° tolerance;[11] thus, we chose a reasonably small Cp_2Ba molecule as a representative example of a bent metallocene. Our GGA calculation gives the bending angle of 144° as compared to the experimental value of 148° for $Ba(C_5Me_5)_2$.

The results presented above indicate that the pseudopotential description of valence electrons distribution is accurate enough to reproduce either sp (linear) or sd (bent) hybridization in Ca-, Sr-, and Ba-containing molecules. It is instructive to note that we explicitly included a nonlocal d component for the Ba pseudopotential, while potentials for Ca and Sr were constructed under the assumption that p and d electrons feel the same potential. The accuracy of the latter approximation is justified by the accurate description of the effect that is known to be based on the differences in sp and sd interactions.

An important factor that guarantees the overall accuracy and transferability of the pseudopotentials for heavy alkaline earth elements is that we include shallow core levels, i.e., $(n - 1)$s and $(n - 1)$p, into the valence shell. This eliminates the problems related to the core polarization and to the nonlinearity of the exchange-correlation potential. The resulting pseudopotentials are highly transferable and can be used in either an ionic, a covalent, or a metallic environment.

To summarize, the total energy pseudopotential method is sufficiently universal and robust to reproduce the ground state structure of alkaline earth dihalides at a fraction of cost of fully *ab initio* techniques. The GGA results are in systematically better agreement with experimental data than are the LDA ones. The final conclusion is that the computational scheme that is based on pseudopotentials and plane-wave basis implementation of the DFT is sufficiently accurate to predict the correct geometry of chosen molecules in all cases where the 0.01 eV accuracy was sufficient to distinguish between bent and linear molecular shapes.

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