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A Test of the Utility of Plane Waves for the Study of Molecules from First Principles

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Abstract: This paper studies the applicability of a plane-wave basis set for density functional calculations of the properties of molecules from first principles. The main features of the plane-wave method are described, including pseudopotentials and supercells. The results for a number of small molecules are reported. The close agreement with experiment and with a standard method of quantum chemistry calculation indicates the promise which this method holds for chemical and biochemical first-principles computations.

I. Introduction

Density functional theory^{1,2} has recently shown significant promise^{3,4} as an analytical tool for studying chemical systems from first principles. Currently, the calculations of properties of molecules containing first-row elements are most commonly performed using a basis set of localized orbitals for wave function expansions. The purpose of this paper is to report results which indicate the viability of the plane-wave basis set as an alternative choice for this expansion. First we will describe the salient features of this computational method, and then we will exhibit structural results for a number of small molecules.

The plane-wave basis set has a number of extremely desirable features. The set of plane waves is complete and orthonormal. In addition, plane waves can be indexed by a single vector index, the wave vector. These two properties make finite sets of plane waves systematically improvable in a straightforward manner. A calculation is performed using a basis set of all plane waves such that each plane wave's wave vector has a magnitude less than some value, the plane-wave cutoff. Then the basis set is improved by increasing the plane-wave cutoff until the results converge.^{5,6} This systematic improvability provides another advantage, the numerical stability of results. Another benefit of using plane waves is that a priori knowledge of the electronic distribution is not required for the generation of the basis set. Finally, there are reliable and efficient methods for finding electronic eigenstates and atomic positions. The Car and Parrinello molecular dynamics method,^{7,8} because it allows simultaneous updates to wave functions and atoms, speeds up calculations significantly relative to traditional matrix diagonalization approaches. The fast Fourier transform algorithm improves the scaling of many parts of the calculation, and the conjugate gradient technique^{9,10} for minimizing the electronic energy makes possible the study of large molecules, whereas other minimization techniques exhibit instability as the cell size becomes very large. The scaling behavior of the various parts of the calculation is shown in Table I. A gauge of the computational time for this method is the time required to calculate the total energy and quantum-mechanical forces on the ions in a particular geometry. For the formamide molecule in a 7-Å box with a plane-wave cutoff of 544.232 eV (40 Ry), this cal-

Table I. Scaling Properties of the LDAP-PW Method^a

step	scaling
Fourier transform of wave functions	$N_b N_{pw} \ln(N_{pw})$
acceleration of coefficients	$N_b N_{pw} \ln(N_{pw})$
forces on ions	$N_b N_i N_{pw}$
orthogonalization	$N_b N_b N_{pw}$

^a N_b is the number of filled bands (orbitals), N_i is the number of ions, and N_{pw} is the number of plane waves. N_{pw} is roughly 100 times larger than N_b , which is twice the size of N_i .

ulation requires approximately 450 CPU s on a Cray-2 computer.

The chief difficulty with using plane waves as a basis set is that sharply-peaked functions require huge numbers of plane waves to converge. For this reason, expression of core electrons using plane waves is extremely difficult. Because valence electrons are orthogonalized to the core, even the expression of valence electrons is very difficult when core electrons are included in the calculation. This problem has been surmounted by the use of pseudopotentials.^{11,12} A pseudopotential is a weaker potential than the Coulomb potential, and it includes the effects of the core electrons implicitly. To generate a pseudopotential, a density functional calculation is normally performed on a free atom with specified electron fillings of the orbitals. A pseudopotential is then con-

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structured so that, outside the core region, its lowest eigenfunctions, called pseudo wave functions, are identical to the valence wave functions of the atomic calculation,¹³ and corresponding states have identical eigenvalues. The pseudopotential is also designed to reproduce the scattering properties of the atomic potential as accurately as possible.¹⁴ Once it is designed with reference to an atomic density functional calculation, the pseudopotential is used without modification in any chemical environment. The pseudopotential approximation is motivated by the observation that valence electrons account for all chemical properties of atoms to a very large extent. Some core relaxation is neglected by this approach, but generalization of the pseudopotential approximation can include this effect, and for many chemical systems of interest, the core relaxation effect is indeed negligible. Thus, the pseudopotential approximation greatly reduces the plane-wave requirements, making density functional calculations with plane waves tractable and leaving the vital chemical interactions intact.

Although pseudopotentials provide a huge gain in computational efficiency, the elements in the first row of the periodic table are still very difficult to describe with plane waves, and for this reason very few plane-wave pseudopotential calculations have been performed on materials containing these elements. Recently, significant advances have been made toward making pseudopotentials for these elements which give converged results with a lower plane-wave cutoff.^{15,16} We use pseudopotentials which are designed to give the most convergent results possible and still provide accuracy^{17,18} using the efficient nonlocal pseudopotential form of Kleinman and Bylander.¹⁹ These pseudopotentials increase computational efficiency sufficiently to allow calculation of the properties of fairly large molecules. Recent generalizations of the pseudopotential form²⁰ hold great promise that even more efficient pseudopotentials will be available in the near future.

Another difficulty with plane waves is that they enforce a periodicity not present in most molecules. A plane-wave basis set is directly applicable to systems which exhibit discrete translational symmetry, so the plane-wave pseudopotential method has been used extensively for crystalline materials. The supercell method greatly expands the class of materials which can be studied with plane waves. In this method, an aperiodic system is placed at each site of a three-dimensional lattice of points, thereby restoring periodicity. In the limit that the lattice points are extremely far apart, the aperiodic system is modeled accurately. Computationally, one systematically increases the lattice spacing and filters out the effects of the induced periodicity.²¹

Because the plane-wave pseudopotential method has a number of positive features as described above, we wish to examine whether it is a viable alternative method for performing high-level *ab initio* quantum chemistry calculations.²²⁻²⁶ This involves testing the ability of pseudopotentials to provide accurate results for first-row atoms, the ability of plane waves to describe the valence wave functions efficiently, and the ability of the supercell method to mimic an isolated system. All of these computational aspects are

completely independent of the exchange-correlation functional, and so for simplicity, we use a local density approximation^{27,28} to this functional. For more realistic calculations, we must use a more accurate functional, but the performance of the LDAP-PW (local density approximation, pseudopotential, plane-wave) method will permit us to gauge the effectiveness of pseudopotentials, plane waves, and supercells.

II. Computational Methods

We generated pseudopotentials according to the methods described above and tested their convergence properties. All pseudopotential calculations of structural parameters were very well converged using a plane-wave cutoff of 544.232 eV. For example, increasing the cutoff to 816.348 eV changed the $\angle(\text{OCN})$ of formamide by less than 0.1° , and the $r(\text{CO})$ and $r(\text{CN})$ distances changed by 0.001 and 0.013 Å, respectively. The accuracy of the pseudopotentials was also tested by calculating their scattering properties and by comparing energy differences between different atomic electronic filling states with the same energy differences evaluated by all-electron density functional calculations. An exception is to be noted in the case of hydrogen. Because it has no core electrons, we used the Coulomb potential to represent the hydrogen nucleus.

We tested the supercell method in two ways. We calculated structural properties of a particular molecule with a certain lattice spacing, and then we repeated the calculation with a larger spacing. We found that as long as the lattice is large enough so that the van der Waals radii of the molecule do not overlap with those of the neighboring molecules, the results are completely insensitive to lattice spacing. For example, increasing the box size of formamide from a 7-Å cube to a 9-Å cube changed the $\angle(\text{OCN})$ by 0.1° , the $r(\text{CO})$ distance by 0.001 Å, and the $r(\text{CN})$ distance by 0.004 Å. In addition, we studied the effect of changing the orientation of the molecules with respect to the translation axes. Here again, as long as the molecules are well-separated, the change in structural parameters when the molecules are reoriented is minimal. Again taking the formamide example, we find that a 30° rotation of the molecule changed the bond angle by less than 0.1° and the bond distances by less than 0.001 Å. One difficulty arises when molecules are placed on a lattice. Even though no chemical bonding takes place between neighboring molecules, and the bonds and angles are unaffected by periodicity, the long-range dipole-dipole interactions slow down the calculations. All the molecules on the lattice rotate to make their dipole moments align. These large-distance (sometimes several angstroms) motions to satisfy spurious intermolecular forces are much more time-consuming computationally than the desired adjustments to attain the proper intramolecular geometry. We have tested that the calculated properties of the molecule are the same in any orientation. Therefore, we inhibit rotation of the molecule as a whole by the following procedure. We compute the quantum-mechanical forces on all the nuclei. We keep one atom fixed at a point. We constrain a second atom to move only on a particular line which passes through the first atom, and we force a third atom to move only within a plane which passes through the first two atoms. All other atoms are free to follow the quantum-mechanical forces without restriction. This allows all interatomic distances and angles to optimize freely, but it prevents rigid rotation of the molecule.

To determine whether the LDAP-PW method and generalizations of it hold promise for quantum chemistry, we calculated structural properties of a number of small molecules. The calculations were done at a 544.232-eV plane-wave cutoff (with the exception of H_2 , which was done at 816.35 eV) and supercell sizes of $5.5 \text{ \AA} \times 5.5 \text{ \AA} \times 5.5 \text{ \AA}$ (4800 plane waves), $7 \text{ \AA} \times 7 \text{ \AA} \times 7 \text{ \AA}$ (9900 plane waves), or $11 \text{ \AA} \times 7 \text{ \AA} \times 5 \text{ \AA}$ (11 100 plane waves), depending on the molecule studied. The electronic degrees of freedom were relaxed until the total energy of the molecule was within 10^{-4} eV/molecule of the converged value. Molecular geometries were considered to be converged when forces on the atoms were less than 0.01 eV/\AA ; optimizations beyond this level changed structures by less than 1%. Initial starting configurations for H_2O , CH_4 , and NH_3 were such that the hydrogen atoms were placed at right angles to one another and a distance of about 1.0 Å from their associated heavy atom. The initial coordinates for all other molecules were taken from AM1 semiempirical calculations using the MOPAC²⁹ program.

III. Results and Discussion

Table II lists the results of the calculations and compares them with both experimental values and MP2/6-31G*, MP2/6-31+G*, or MP2/6-31G** Hartree-Fock³⁰ calculations. Overall agreement

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Table II. Comparison of LDAP-PW Geometry Optimizations with Experiment and with MP2^a

molecule	parameter	expt	MP2	Δ_1^1	LDAP-PW	Δ_2^2	Δ_G
H ₂	r(HH)	0.742	0.738	0.004	0.776	0.034	0.038
O ₂	r(OO)	1.208	1.242	0.034	1.183	0.025	0.059
N ₂	r(NN)	1.098	1.131	0.033	1.099	0.001	0.032
P ₂	r(PP)	1.893	1.936	0.043	1.875	0.018	0.061
CO	r(CO)	1.128	1.151	0.023	1.138	0.010	0.013
CO ₂	r(CO)	1.162	—	—	1.170	0.008	—
H ₂ O	r(OH)	0.958	0.969	0.011	0.976	0.018	0.007
	∠(HOH)	104.5	104.0	0.5	104.0	0.5	0.0
CH ₄	r(CH)	1.092	1.090	0.002	1.102	0.010	0.012
NH ₃	r(NH)	1.012	1.017	0.005	1.028	0.016	0.011
	∠(HNH)	106.7	106.3	0.4	105.7	1.0	0.6
PH ₃	r(PH)	1.420	1.415	0.005	1.440	0.020	0.025
	∠(HPH)	93.3	94.6	1.3	91.6	1.7	3.0
H ₂ O ₂	r(OO)	1.452	1.467	0.015	1.414	0.038	0.053
	r(OH)	0.965	0.976	0.011	0.982	0.017	0.006
	∠(OOH)	100.0	98.7	1.3	100.2	0.2	1.5
	∠(HOOH)	119.1	121.3	2.2	118.7	0.4	2.6
N ₂ H ₂	r(NN)	1.252	1.267	0.015	1.233	0.019	0.034
	r(NH)	1.028	1.036	0.008	1.052	0.024	0.016
	∠(NNH)	106.9	105.4	1.5	107.2	0.3	1.8
H ₂ CO	r(CO)	1.208	1.221	0.013	1.205	0.003	0.016
	r(CH)	1.116	1.104	0.012	1.135	0.019	0.031
	∠(HCH)	116.5	115.6	0.9	116.4	0.1	0.8
C ₂ H ₂	r(CC)	1.203	1.218	0.015	1.196	0.007	0.022
	r(CH)	1.061	1.066	0.005	1.058	0.003	0.008
HNC	r(NC)	1.169	1.187	0.018	1.178	0.009	0.009
	r(HN)	0.994	1.002	0.008	1.018	0.024	0.016
HNO	r(NO)	1.212	1.237	0.025	1.188	0.024	0.049
	r(HN)	1.063	1.058	0.005	1.093	0.030	0.035
	∠(HNO)	108.6	107.3	1.3	109.2	0.6	1.9
formamide (HCONH ₂)	r(CO)	1.193	1.224	0.031	1.217	0.024	0.007
	r(CN)	1.376	1.361	0.015	1.365	0.011	0.004
	∠(OCN)	124.7	124.8	0.1	124.9	0.2	0.1
glycine (NH ₂ CH ₂ CO ¹ O ² H)	r(C=O ¹)	—	1.218	—	1.204	—	0.014
	r(CO ²)	—	1.358	—	1.345	—	0.013
	r(CC)	—	1.515	—	1.535	—	0.020
	r(NC)	—	1.451	—	1.460	—	0.009
	∠(O ¹ CO ²)	—	123.2	—	123.7	—	0.5
	∠(O ² CC)	—	111.4	—	111.9	—	0.5
	∠(O ¹ CC)	—	125.4	—	124.4	—	1.0
	∠(CCN)	—	114.9	—	114.8	—	0.1
H ₂ PO ₄ ⁻	r(PO)	—	1.510	—	1.482	—	0.028
	r(P-OH)	—	1.680	—	1.640	—	0.040
	∠(HO-P-OH)	—	101.1	—	101.2	—	0.1
	∠(O-P-OH)	—	106.9	—	107.1	—	0.2
	∠(O-P-O)	—	126.2	—	125.2	—	1.0
3-hydroxyacrylaldehyde (HOCHCHCHO)	r(O-H)	0.969	0.994	0.025	1.079	0.110	0.085
	r(O...H)	1.680	1.694	0.014	1.418	0.262	0.276

^a All experimental and MP2 values are taken from ref 30 except those of glycine, H₂PO₄⁻, and 3-hydroxyacrylaldehyde,^{34,35} which were optimized using Gaussian 90 at MP2/6-31G*, MP2/6-31+G*, and MP2/6-31G**, respectively. Δ_1^1 and Δ_2^2 are the deviations of the MP2 and LDAP-PW calculations from experiment, and Δ_G is the deviation of LDAP-PW from the MP2 values.

of LDAP-PW with experiment and MP2 calculations is excellent. Average deviations from experiment and MP2 are 0.030 and 0.034 Å for bond lengths and 0.5° and 1.0° for bond angles. These results also compare favorably with localized orbital density functional methods. Reference 3 lists several practical examples. If the hydrogen-bonded system 3-hydroxyacrylaldehyde is not included in the averages, the bond-length deviations become 0.017 and 0.024 Å, respectively. Upon closer examination, certain trends become apparent within the data contained in Table II. The most striking pattern is that an LDAP-PW calculation of a bond distance between two heavy (non-hydrogen) atoms is almost always closer to experiment than the corresponding MP2 result. Conversely, bonds involving at least one hydrogen are almost always calculated more accurately using MP2. In addition, bond angles which include zero or one hydrogen atom are almost always more accurate using LDAP-PW, while those including two hydrogens are usually better reproduced by MP2. We believe that these effects are due to the use of the LDA rather than a more accurate exchange-correlation functional. The small size of hydrogen makes

its charge density change over a short length scale. Another trend which we have observed is that long bonds are reproduced more poorly than short bonds by the LDAP-PW. As the atoms in a bond separate, they act more like free atoms, and the LDA does a poorer job on free atoms than on covalent materials.³¹ This effect is apparent in the O-O bond of H₂O₂ and the hydrogen bond in 3-hydroxyacrylaldehyde. The most striking deviation from MP2 and from experimental results is the internal hydrogen bond in 3-hydroxyacrylaldehyde. The LCGTO-MCP-LSD method gave an O-H distance of 1.228 Å for this molecule (referred to as malonaldehyde in ref 3). Our result of 1.418 Å is closer to experiment, but it is still 0.262 Å from the experimental value of 1.68 Å. The use of the plane-wave basis set provides accurate solution of the density functional equations, and the inadequacy in the local density approximation appears to be the main barrier to more highly accurate calculations. Work is in progress to incorporate nonlocal corrections.^{32,33}

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IV. Conclusions

These results show that the LDAP-PW method can produce accurate structural parameters for molecules. The data suggest that the method which uses plane waves, pseudopotentials, and supercells may be a useful alternative to standard ab initio quantum-mechanical methods for calculations on chemical systems. Future work will include more realistic density functionals and tests of energetics of chemical transformations. In addition, research is continuing to develop more efficient energy mini-

mization algorithms and superior pseudopotentials. These changes will improve the efficiency and accuracy of the method for the study of periodic and aperiodic chemical and biochemical systems.

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Ab Initio Prediction of the Structure and Stabilities of the Hypermagnesium Molecules: Mg₂O, Mg₃O, and Mg₄O

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Abstract: The concept of hypermetalation, characterized by molecules with unprecedented stoichiometries, is extended to the magnesium-oxygen combinations, Mg₂O, Mg₃O, and Mg₄O. Their equilibrium geometries and fundamental frequencies were calculated at the HF/6-31G* and correlated MP2 (full)/6-31G* levels. Extensive searches of possible structures and electronic states were carried out. The global minima are as follows: linear Mg₂O (*D*_{∞h}, both singlet ¹Σ_g⁺ and the triplet ³Σ_u⁻ states), planar Mg₃O (*D*_{3h}, ³A₁[']), and Mg₄O forms slightly distorted from the square planar arrangement (*D*_{2d}, ¹A₁ and planar MgOMg₃ (*C*_{2v}, ¹A₁) structures have nearly the same energy). These Mg₂O, Mg₃O, and Mg₄O species are stable with regard to all possible decomposition pathways. Representative dissociation energies are the following: Mg₂O, 74.5 kcal/mol into MgO + Mg at QCISD (T)/6-311+G(3df)+ZPE; Mg₃O, 26.7 kcal/mol into Mg₂O + Mg at QCISD(T)/6-311+G*+ZPE; and Mg₄O, 7.9 kcal/mol into Mg₃O + Mg at MP4SDTQ/6-311+G*+ZPE. Magnesium-magnesium bonding contributes significantly to the stability of Mg₃O and Mg₄O.

Introduction

Hypermetalation, involving metal stoichiometries exceeding normal valence expectations, should be a general phenomenon exhibited by many if not all metals. Hyperalkali metal molecules are now well-documented. Many hyperlithium molecules, OLi₄, OLi₅, OLi₆, NLi₅, CLi₅, OLi₆, BLi₅, BeLi₄, BeLi₅, etc., were discovered by calculation.¹⁻⁹ Li₃O, Li₄O, and Li₅O have been observed by mass spectrometry and atomization energies determined.^{10,11} There is similar evidence for Na₂Cl,¹² Na₃O, Na₄O, K₃O, K₄O,^{13,14} and Cs₈O.¹⁵ The "suboxides" of rubidium and cesium, e.g., Rb₂O₂, Cs₇O, and Cs₁₁O₃, have been characterized.^{16,17} Bonding interactions between ligand atoms contribute to both the structure and the stability of these species.¹⁻⁹ Despite

having the usual stoichiometry, SiLi₄ also is instructive. Metal-metal bonding contributes to the surprising preference for a

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