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Augmented-plane-wave calculations on small molecules

P. A. Serena* and A. Baratoff
IBM Research Division, Zürich Research Laboratory, CH-8803 Rüschlikon, Switzerland

J. M. Soler
Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

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We have performed *ab initio* calculations on a wide range of small molecules, demonstrating the accuracy and flexibility of an alternative method for calculating the electronic structure of molecules, solids, and surfaces. It is based on the local-density approximation (LDA) for exchange and correlation and the nonlinear augmented-plane-wave method. Very accurate atomic forces are obtained directly. This allows for implementation of Car-Parrinello-like techniques to determine simultaneously the self-consistent electron wave functions and the equilibrium atomic positions within an iterative scheme. We find excellent agreement with the best existing LDA-based calculations and remarkable agreement with experiment for the equilibrium geometries, vibrational frequencies, and dipole moments of a wide variety of molecules, including strongly bound homopolar and polar molecules, hydrogen-bound and electron-deficient molecules, and weakly bound alkali and noble-metal dimers, although binding energies are overestimated.

I. INTRODUCTION

With the prodigious pace of improvement in computer hardware and software, computer-assisted drug design is rapidly becoming a reality, allowing the microscopic simulation of the chemical binding and action of key molecular units. Generally, the codes which have allowed such complex simulations are based on empirical short-range potentials which parametrize the most essential forces due to bond stretching, bending, and torsion, plus a simpler parametrization of weaker, longer-range interactions. However, in situations where bonds are broken or where unusual binding configurations occur, such as when an energy barrier is crossed, empirical potentials are difficult to fit and much less reliable. This is also the case when very small energy differences are critical, as when different molecular foldings are compared. In these cases, it would be highly preferable to obtain atomic forces from first principles. This is not only because of the increased accuracy of *ab initio* methods: if we systematically obtain very accurate results for a wide range of chemical systems and configurations without any recourse to parameter fitting, we will be more confident with calculations for other systems and configurations where comparison with experiment is difficult or impossible. Of course, *ab initio* methods are much more demanding but, given the rate of increase in computer capacity, this only means a few years lag. Also, dramatic progress has been achieved in the past few years in improving *ab initio* algorithms. In particular, the Car-Parrinello method of *ab initio* molecular dynamics[1] has demonstrated the possibility of simulations with more than 100 atoms moving during several picoseconds.[2] This method is based on the local-density approximation (LDA) for exchange and correlation[3,4] in the framework of the density-functional theory (DFT),[5,6] and, in its most widespread implementation, uses a plane-wave basis set together with *ab initio* pseudopotentials.

Despite its apparent crudeness, over the last 20 years the LDA has proven impressively accurate and versatile for a vast number of systems (pure and defective ionic, covalent, and metallic solids, surfaces, clusters, molecules. etc.), and properties (geometries, structural energy differences, activation barriers, vibrational frequencies, electronic states and bands, magnetism, etc.).[7,8] There is some evidence that this success is partly due to a partial cancellation of errors, with underestimated exchange and overestimated correlation, but, since these two energies are treated on the same footing, the distinction is partly academic. The resulting method has proven remarkably economical and reliable. In fact, it has proven on the whole more reliable than the much more "expensive" Hartree-Fock (HF) method, because of the approximate inclusion of electron correlation. One drawback is that, in contrast to configuration interaction (CI) improvements of the HF solution, the LDA method has no systematic extension, and many of the proposed improvements have not fulfilled their expected promise. However, some recent approaches[9,10] do seem to provide systematic improvements at a reasonable cost. And, in any case, the original LDA is already remarkably accurate for many properties of different systems. Thus, equilibrium interatomic distances are typically given within 1–2% of experiment, binding energies within 20%, vibration frequencies within 5%, and energy differences between similar configurations within 0.1 eV. As a matter of fact, it has been frequently recognized that other more "technical" problems, such as the quality of the basis set and the accuracy of the potential, can easily introduce larger errors than the LDA itself. Therefore, we think it worthwhile to present a survey of representative chemical

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systems exhibiting different kinds of binding, and treated by the same computationally very accurate method based on the LDA. This is the aim of the present paper. We have used an implementation of the augmented-plane-wave (APW) method with Car-Parrinello-like features applicable to bulk systems, surfaces, and molecules with arbitrary constituents (at least in principle, since spin and relativistic effects must still be incorporated). As with pseudopotential methods, it relies on plane waves to expand the wave functions and the effective potential over most of space. This ensures an unbiased basis set, equally valid for any molecular arrangement, and whose completeness is guaranteed and simply controlled by increasing the number of plane waves included in actual computations. The risk of using insufficient bases in special cases involving very weak, highly delocalized, or stretched bonds is thus eliminated. At the same time, being an all-electron method, it avoids the uncertainties of pseudopotential generation and transferability. We would like to stress that the method and *the code* are exactly the same as those used for bulk systems;[11] only the input data file which specifies the atomic positions must actually be changed. This offers the possibility of easily extending the calculations to atoms or molecules absorbed on a surface and to molecular-solid phases, although in the present work we have limited ourselves to free molecules in the gas phase.

We have applied this method to homopolar diatomic molecules of first-row and columns IA, IB, and IIB atoms exhibiting strong to very weak covalent bonds, to heteropolar diatomic molecules with weak to strong ionic character, to multiatomic bent and nonplanar molecules with localized bonds, "lone electron pairs," and dipole moments, as well to as larger molecules with delocalized bonds, and to a hydrogen-bonded dimer. We focus our attention on equilibrium molecular geometries, binding energies, vibrational frequencies, and electric dipoles rather than on electronic (spectroscopic) properties because our main goal is to validate our method and to provide further evidence for the overall success and occasional deficiencies of the LDA, with an eye toward the possibility of *ab initio* molecular dynamics and simulation of complex interactions of large molecules in the not-so-distant future.

We have little to add to the semiquantitative insight into different kinds of bonding and into the trends shown by the above-mentioned measurable properties which is provided by molecular orbitals at the minimal basis linear combination of atomic orbitals (LCAO) level as described in many excellent quantum chemistry textbooks. Calculated values typically depend on partial cancellation between several contributions affected by subtle quantitative features of the self-consistent molecular orbitals which have no simple interpretation or have already been amply discussed in the literature, e.g., in Refs. 6, 8, and 12. Spin polarization has so far been taken into account, through the local-spin-density (LSD) approximation,[13] only for isolated atoms because it usually makes only a minor contribution to the total energy of most molecules and has a negligible influence on molecular geometries. This small effect has been noticed in previous calculations[14] for first-row diatomic molecules, in which the computational procedure for solving the effective one-electron problem was fixed for three different exchange-correlation functionals. Results showed that there is (in average on several molecules) a change of only 1% in the bond lengths, 12% in the binding energies, and 5% in the vibrational frequencies when the exchange-correlation functional is modified from the crude $X\alpha$ model of Slater[15] to the LSD approximation.[13] Although differences for binding energies seem to be quite high, it has been noticed[8,12,14] that even the LSD approximation fails by almost 20% to reproduce experimental results. Therefore numbers which concern the binding energy must be handled with caution in any *local* approximation.

II. METHOD OF CALCULATION

The use of a finite discrete basis of plane waves implies periodicity. When this periodicity does not naturally exist, as in the case of free molecules or clusters, it must be artificially generated by placing the system at hand in a large enough "supercell" and applying periodic boundary conditions. In the present calculations we have used simple cubic cells, which have the advantage of ensuring exact cancellation of residual interactions between replicated molecules with dipoles oriented along a principal axis.[16] The size of the unit cell is increased until none of the computed quantities changes significantly. When the cell is large, the corresponding reciprocal-space unit cell (Brillouin zone) becomes small and any wave vector $\mathbf{k}$ contained in it should yield the same results. In other words, the relative phase of the wave functions in different cells become irrelevant if the systems replicated in adjacent cells are so well separated that their interaction becomes negligible. Therefore, it seems that a logical strategy only would make use of $\mathbf{k}=\mathbf{0}$ (the Γ point). In this case, the wave functions may be chosen to be real, thus avoiding complex arithmetic and saving computer time.[17] In practice, however, we have found that the use of a "special point",[18] which represents a better average over the Brillouin zone, makes the results converge much faster with increasing cell size, more than compensating for the need of complex arithmetic. Generally, a distance between molecules of 8 a.u. is sufficient to make the total energy converge to 1 mRy, although we have used up to 25 a.u. in specific cases (large bond lengths or large dipole moments).

A basis set of plane waves is totally inadequate to represent the rapid oscillations of the wave function near any nucleus. A widespread solution is to replace the true potential in this region by a hopefully smoother "pseudopotential"[19] with the same scattering properties in the energy range of the valence states. To achieve this without losing accuracy, the pseudopotential must be nonlocal (angular-momentum-dependent). Furthermore, it must be "norm conserving" so that the integrated absolute square of each occupied pseudo-wave-function over the cell is equal to that of the true wave function. In the case of first-row and transition-metal constituent atoms, owing to strong p or d pseudopotential components, the requirement of norm conservation implies that even the valence pseudo-wave-functions vary too rapidly to be efficiently represented with plane waves. A solution to this problem has recently been proposed[20,21] with new types of pseudopotentials which relax the norm-conservation condition. Another, more conventional solution, which we adopt here, is the augmented-plane-wave (APW) method, initially proposed by Slater[22] and later improved by Anderson[23] and others.[24,25] The present implementation of the APW method[11,26] includes the following improvements.

(i) The nonspherical components of the potential, and the high-angular-momentum components of the wave functions close to the atoms, are represented by plane waves. This ensures that they are strictly continuous and smooth across the muffin-tin-sphere surface (see below), and allows a substantial reduction of the maximum angular momentum involved in the "augmentation" procedure. In addition, this permits an adequate description of strong localized and directed covalent bonds such as those of carbon atoms.

(ii) The use of Car-Parrinello-like iterative techniques in the solution of Schrödinger's equation enables us to avoid the diagonalization of large matrices to find the eigenvalues of the relevant states. As a consequence, the linear approximation to the energy dependence of the wave functions, which was useful in the context of diagonalization,[23] is no longer necessary.

(iii) A convenient analytic expression for the force on any given nucleus has been derived within the present formulation[11] and demonstrated to be quite accurate.[26] This is a prerequisite for the simultaneous self-consistent determination of electronic eigenstates and nuclear positions.[1,26]

As in APW and related methods, space is divided into nonoverlapping "muffin-tin" spheres, centered on every nucleus, and into the remaining "interstitial" space which, in our case, includes the vacuum region surrounding the molecule in each cell. In the interstitial region, the wave functions and the potential are represented with plane waves:

$$V(\mathbf{r})=\tilde{V}(\mathbf{r})=\sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} , \tag{1}$$

$$\psi(\mathbf{r})=\tilde{\psi}(\mathbf{r})=\sum_{\mathbf{G}} \psi_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} , \tag{2}$$

where G's are the reciprocal-lattice vectors corresponding to the artificial lattice of periodically repeated cells, and we consider only $\mathbf{k}=0$ for simplicity. Inside the muffin-tin spheres, the potential defined by Eq. (1) is "augmented" with the "muffin-tin potential" $V_0(r)$ (the spherical average of the true potential inside the spheres), calculated on a radial mesh:

$$V(\mathbf{r})=\tilde{V}(\mathbf{r})+V_0(r)-\tilde{V}_0(r) , \tag{3}$$

where $\tilde{V}_0(r)$ is the spherical average of $\tilde{V}(\mathbf{r})$. Analogously,

$$\psi(\mathbf{r})=\tilde{\psi}(\mathbf{r})+\sum_{l=0}^{l_{\max}}\sum_{m=-l}^{l}[\psi_{lm}(r)-\tilde{\psi}_{lm}(r)]Y_{lm}(\hat{r}) , \tag{4}$$

where $\tilde{\psi}_{lm}(r)$ is the component with angular momentum lm of the "smooth" part of the wave function [defined in Eq. (2)], and $\psi_{lm}(r)$ is a numerical radial solution of Schrödinger's equation for the muffin-tin potential $V_0(r)$. The energy of this numerical solution is chosen, for each lm, so that it matches the smooth part $\tilde{\psi}_{lm}(r)$ in value and slope, at the muffin-tin-sphere radius. The use of $\tilde{\psi}(\mathbf{r})$ to represent the high angular momentum of the wave functions inside the muffin-tin spheres (rather than just neglecting them) allows us to reduce the value of $l_{\max}$ to the chemically relevant values, i.e., $l_{\max}=0$, 1, and 2 for *s*-, *p*-, and *d*-block atoms, respectively, instead of retaining higher values typical of other APW implementations.

On the other hand, a well-established APW rule to set the number of required plane waves is given by $G_{\max}R_{\min}=5+l_{\max}$, where $R_{\min}$ is the radius of the smallest muffin-tin sphere and $G_{\max}$ is the maximum wave vector to be included. Since first-row molecules have very short bonds and the muffin-tin spheres cannot overlap, $R_{\min}$ must be chosen to be small and $G_{\max}$ to be very large for such systems. In practice, this means that several thousand plane waves are required to obtain total energies converged to 1 mRy. Surely enough, other properties, such as molecular geometries, vibrational frequencies, electric dipoles, and barrier heights, are well converged with far fewer plane waves, but we have always imposed the 1-mRy criterion for the convergence of the total energy in order to provide very reliable binding energies.[27]

Such plane waves treat all regions of space equivalently, offering the same precision in regions where the wave functions are large or exponentially small. Since most of the space in the unit cell is empty, a plane-wave basis seems especially inappropriate for describing the wave functions of isolated molecules or clusters. Indeed, as already mentioned, even with the augmentation method, we typically need several thousand plane waves for a first-row diatomic molecule. This is to be compared with a localized basis set, which would typically contain at most a few tens of analytic functions, e.g., Gaussians, to represent each atomic orbital. Part of the price is paid by the intrinsic simplicity of plane waves and by the ability of fast Fourier transforms (FFT) to speed up the calculation of matrix elements. In order to further decrease the computational effort, we rely on an iterative approach[26] to solve Schrödinger's equation, similar to that used by Car and Parrinello:[1] the total energy is minimized by a preconditioned steepest-descent method, as a function of all the plane-wave coefficients, while imposing the required orthonormalization constraints. The computation time of this method scales as $NM\ln M+N^2M$, where N is the number of electrons and M is the (much larger) number of plane waves. This is to be compared with M^3 for the traditional Rayleigh-Ritz method, which involves the diagonalization of an $M\times M$ secular matrix. Moreover, the required amount of computer memory decrease from M^2 to NM. Although we have not done any molecular-dynamics simulations in this work, a crucial advantage is that the method allows the simultaneous relaxation of the electronic and nuclear degrees of freedom. The nuclei are moved according to the computed forces[26] and, once self-consistency is achieved, they are on the Born-Oppenheimer surface, i.e., in their equilibrium positions when the forces become vanishingly small.[11] In order to find the vibrational normal modes, the Hessian matrix of second derivatives is computed by displacing each atom by ±0.1 a.u. in each Cartesian direction and repeating the self-consistency iteration for each of these atomic positions.[28,29] Because the atomic displacements are small, the wave functions at the equilibrium positions can be used as an initial guess and much fewer iterations are required.

The calculation of electrostatic dipoles with a repeated-cell geometry requires some caution: if the electronic charge density is not exactly zero at the unit-cell boundaries, small changes in the origin of coordinates may lead to very large changes in the dipole. To avoid this artifact, we consider a sphere around the molecule and move it to minimize the electronic charge left outside. Then, if we use its center as the origin of coordinates, the electrostatic dipole is already well converged for cell sizes of about 8 a.u. In the case of elongated or strongly polar molecules, we have checked the dipole obtained with this method by repeating the calculation in unit cells with lattice constants up to 20 a.u. The combination of a large unit cell and a large plane-wave cutoff (mainly determined by the small muffin-tin radii) leads to an important time cost per iteration step. Fortunately, in general, only 80–100 iterations are needed to reach an extremely good convergence for all the properties of interest, thus keeping the total computational time within reasonable limits.

Finally, we point out that the calculations were performed within the LDA using the parametrization proposed by Hedin and Lundqvist[30] for describing exchange and correlation. The use of a different parametrization, e.g., Ref. 9, does not significantly modify the calculated molecular geometries or the vibrational frequencies, although it may slightly affect binding energies.

III. RESULTS

In this section, we present our APW results for small molecular systems, paying attention mainly to equilibrium configurations, binding energies, vibrational frequencies, and electrostatic dipole moments, and comparing with other theoretical and experimental results. Due to the wide variety of systems considered, we have selected representative values obtained with different theoretical tools rather than attempting to make an exhaustive survey.

The first application has dealt with first-row diatomic molecules (H_2, B_2, C_2, N_2, O_2, and F_2). These molecules are strongly bound, have short bond lengths, and require expensive calculations with the conventional *ab initio* pseudopotentials,[19] unless limited basis sets are used. In Table I, we compare our equilibrium bond length R_e, binding energy D_e, and vibrational frequency ω_e to the well-established experimental values for each molecule. In all these systems we used small muffin-tin radii (generally less than 1.0 a.u.) and a high plane-wave cutoff of 50 Ry. Tests carried out with a cutoff of 30 Ry showed only a slight change in R_e (0.1%). Agreement for R_e (Refs. 31 and 32) is within 2%, except for H_2, in which case a discrepancy of almost 5% is found. Vibrational frequencies are obtained within 1%, except for H_2 (5%) and F_2 (20%). In general, our results reproduce previous LDA calculations quite well[14,33] on these relatively simple systems, characterized by covalent bonding. Binding energies show a large relative error (10–20 %), by now a well-known failure of the LDA.[8,12] This and other discrepancies mentioned above and trends along the series have been thoroughly discussed in the above-mentioned references and in chemistry textbooks, so that we refrain from repeating them here. We only wish to stress that we found no difference between R_e values obtained from fitting a set of static calculations of the total energy and those at the end of a combined steepest-descent procedure for both electrons and nuclei,[26] thus confirming that forces are indeed accurately computed within our APW formulation.

TABLE I. Bond lengths R_e, dissociation energies D_e, and vibrational frequencies ω_e, for first-row homopolar diatomic molecules. Numbers in parentheses give the experimental results (Refs. 31 and 32).

Molecule	R_e (a.u.)	D_e (eV)	ω_e (cm^{-1})
H_2	1.45	4.6	4160
	(1.40)	(4.75)	(4395)
B_2	3.05	3.5	1030
	(3.00)	(3.30)	(1050)
C_2	2.36	7.7	1860
	(2.35)	(6.20)	(1855)
N_2	2.07	11.3	2380
	(2.07)	(9.9)	(2360)
O_2	2.29	6.2	1620
	(2.28)	(5.2)	(1580)
F_2	2.63	3.1	1060
	(2.68)	(1.70)	(890)

A more complete set of calculations was carried out for the two slightly polar first-row diatomic molecules CO and NO, which are also strongly bound through primarily covalent bonds and have a short bond length. Besides R_e, D_e, and ω_e, we have also determined the dipole moment μ_e (at the equilibrium bond length R_e) and its derivative μ'_e with respect to R_e which determines their infrared oscillator strength.[31] A characteristic of these two molecules is that the measured dipole has the opposite direction to what one would expect from the atomic electronegatives. As shown in Table II, our R_e and ω_e values are again remarkably close to experimental ones,[31,32] although a large relative error appears in D_e (from the LDA). In both molecules the calculated direction of μ_e agrees with the experimental one,[34] although a relatively large difference of 0.1 D (Debye) is noticed in its magnitude. These results, however, are similar to pre-

TABLE II. Bond lengths R_e, dissociation energies D_e, vibrational frequencies ω_e, electrostatic dipole moments μ_e, and dipole moment derivatives μ'_e, for CO and NO. Numbers in parentheses give the experimental results (Refs. 31 and 32; μ_e and μ'_e values for CO are from Ref. 34).

Molecule	R_e (a.u.)	D_e (eV)	ω_e (cm^{-1})	μ_e (D)	μ'_e (D/a.u.)
CO	2.14	12.7	2180	-0.22	1.72
	(2.13)	(11.2)	(2170)	(-0.12)	(1.66)
NO	2.17	8.07	1900	-0.31	1.27
	(2.17)	(6.6)	(1904)	(-0.18)	(——)

TABLE III. Bond lengths R_e, dissociation energies D_e, vibrational frequencies ω_e, electrostatic dipole moments μ_e, and dipole moment derivatives μ'_e, for FH and NaCl. Numbers in parentheses give the experimental results (Ref. 31; μ_e values for FH and NaCl are from Refs. 40 and 41, respectively).

Molecule	R_e (a.u.)	D_e (eV)	ω_e (cm^{-1})	μ_e (D)	μ'_e (D/a.u.)
FH	1.76	6.23	3990	1.85	0.95
	(1.73)	(6.12)	(4139)	(1.82)	(——)
NaCl	4.53	4.19	326	9.15	2.15
	(4.46)	(4.22)	(365)	(9.00)	(——)

vious LDA calculations for both molecules.[35] It is worth noting that Hartree-Fock calculations of μ_e in these molecules[35,36] give the wrong dipole direction. Even in very expensive CI calculations, the computed values of μ_e (for CO) range from -0.082 (Ref. 37) to -0.32 D.[38] It has been necessary to use coupled-cluster (CC) methods including all single, double, and triple excitations (perturbatively) to reach an accurate value of μ_e for CO.[39] Furthermore, good agreement with experiment is obtained with out μ'_e value for the CO molecule, similar to a previous LDA study.[35]

Having described molecules characterized by covalent bonding, where the valence charge distribution does not show dramatic variations within the molecule, we applied our method to diatomic molecules with predominantly ionic bonding, in which a considerable amount of electronic charge is surrounding the more electronegative atom, yielding strong variations of the electron density and of the electrostatic potential within the molecule itself. This provides a more severe test of the LDA, which was in principle expected to deal adequately with slowly varying densities. For the same reason, these systems are even less obviously suited for a plane-wave representation, thus offering an additional "challenge" to our APW code. We have performed optimizations for the two molecules FH and NaCl, which were chosen because they have very different properties although their ionic character is dominant. On one hand, the very short bond length in FH forces us to use small muffin-tin radii for both F and H, thus implying a high plane-wave cutoff of 50 Ry. Thanks to the small size of this molecule and the relative weakness of its dipole, an accurate calculation could, however, be carried out using a lattice constant of only 9 a.u. On the other hand, the second-row NaCl molecule contains a much larger number of core electrons, and its much longer bond permits us to choose larger muffin-tin radii and thus to work with a low plane-wave cutoff. In fact, we used 15 Ry, a value far below the high cutoff needed in conventional pseudopotential schemes. Nevertheless, the computer memory requirements are not significantly reduced since the dimensions of the molecule and the strength of its dipole moment make it necessary to increase the lattice constant up to 25 a.u.

Computed and experimental properties of FH and NaCl are compared in Table III. As expected, LDA provides a poorer description of ionic bonding than of covalently bound systems. Bond lengths and dipole moments nevertheless agree with experiment within 2%. Moreover, calculated binding energies are in good agreement with experiment, owing mainly to the electrostatic character of the bond. Poorer accuracy becomes manifest for the vibrational frequency of FH, similar to what is noticed in H_2. At this point we wish to point out that our calculated values (R_e, D_e, and ω_e) are in line with previous local-spin-density approximation (LSDA) calculations on FH.[42] Also, the thoroughly studied dipole moment of FH agrees with other LDA calculations,[43] is much closer to experiment than the high value of 1.98 D obtained from HF computations,[40] and shows a degree of accuracy similar to that obtained from more complex computations such as coupled-cluster methods, many-body perturbation expansions, or the coupled electron-pair approximation reviewed recently by Chong and Langhoff.[44] Our calculated dipole moment for NaCl is slightly lower than that obtained from a numerical Hartree-Fock calculation (9.19 D),[45] following the trend apparent for HF.

Having dealt with some light diatomic molecules, we slightly increased the complexity of the systems studied by performing APW computations for H_2O, NH_3, and O_3. Tables IV, V, and VI summarize our results for the optimized geometrical parameters (bond angles and lengths), as well as for the binding energies, vibrational frequencies, and electrostatic dipole moments. The agreement for the bond lengths is again excellent, with a maximum discrepancy of only 1.2% in the O-O bond lengths of weakly bound ozone. For O_3, we also found the worst result for the bond angle, but this error is below 1% in relation to experiment.[48] By contrast, the strongly overestimated binding energy for O_3 is a particularly dramatic example of the failure of the LDA in a weakly bound system where two configurations compete for the ground state. As discussed by Jones,[51] the LDA nevertheless gives a satisfactory account of the ordering of the lowest electronic states of different symmetry in O_3, as well as its sulphur-substituted homologs. Our APW results are in the same line as (and even slightly improve upon) previous LDA calculations for H_2O,[11,52,53] NH_3,[52,54] and O_3.[51,55] Calculations on these three molecules were carried out using a simple cubic unit cell with a lattice constant of 16 a.u. The plane-wave cutoff was taken to be 50 Ry for the final and more accurate calculation. We remark at this point that there exists a

TABLE IV. Geometrical equilibrium parameters ($d_{\text{O-H}}$ and $\theta_{\text{H-O-H}}$), dissociation energy D_e, vibrational frequencies ω_e, and electrostatic dipole moment μ_e, for water. Experimental results are from Ref. 46.

Molecule		APW	Experiment	
H_2O	$d_{\text{O-H}}$ (a.u.)	1.83	1.81	
	$\theta_{\text{H-O-H}}$	103.9°	104.5°	
	D_e (eV)	11.5	10.08	
	ω_e (cm^{-1})	3600	3657	(a_1) symmetric stretch
		1610	1595	(a_1) bend
		3670	3756	(b_2) antisymmetric stretch
	μ_e (D)	1.79	1.80	

difference of almost 1° in the H_2O bond angle between the present calculation and a previous one reported by Soler and Williams.[11] This is in fact due to the smaller lattice constant (8 a.u.) in their calculation, showing the scale of effects arising from the residual interaction among molecules in neighboring cells. The calculated dipole moments μ_e are in the range of the experimental values;[46,47,50] in the case of H_2O and NH_3, the error remains under 5%, but it increases up to 18% for O_3. Summarizing results obtained for the dipole moments of the polar molecules considered at the present work, we note that our computational scheme is able to determine them with an *absolute* accuracy close to 0.1 D.

The most expensive part of a computation such as ours corresponds to the evaluation of the vibrational frequencies. Fortunately, restoring forces corresponding to particular displacements could be computed directly. Together with the high symmetry of these molecules, a large fraction of time could therefore be saved in determining the dynamical matrix. In general, results agree with experiments within 10%, the absolute error being less than 100 cm^{-1}. The worst result corresponds again to ozone, where the symmetric stretch mode is predicted to lie below its antisymmetric partner, whereas experiment[46] shows the reverse order. We nevertheless can point out that for achieving accurate results through CI calculations in this particular molecule, it has been essential to include perturbatively triple excitations into state-of-the-art coupled-cluster singles and doubles (CCSD) calculations, since otherwise errors larger than 200 cm^{-1} arise.[56,57] In our case even the elusive antisymmetric stretch-mode frequency has been evaluated with an error below 170 cm^{-1}.

A topic of special interest is the determination of the inversion barrier U_i in the NH_3 molecule. We have first optimized the planar ammonia configuration, obtaining a N-H distance of 1.91 a.u., that is, 0.03 a.u. lower than that calculated in the nonplanar optimized equilibrium geometry. The difference in energy between these two configurations is 0.19 eV, this amount being close to that from previous LDA calculations,[52,54] and somewhat lower than the experimental value of 0.25 eV.[46,58] A recent study of the origin of the inversion barrier in NH_3 from the CI perspective yields a change of 0.025 a.u. in the N-H distance, very similar to our prediction, and a better value of 0.23 eV for the inversion barrier,[59] although the CI equilibrium geometry for NH_3 is worse (1.89 a.u. for the N-H distance and a H-N-H angle of 108°) than that obtained within the LDA.

Up to now we have described results obtained on small molecules characterized by predominantly covalent or ionic bonding. In a major step to test the performance of LDA in predicting more complex structures, we applied our APW method to benzene (C_6H_6) and diborane (B_2H_6). These two molecules were chosen for the following reasons: (i) they involve more atoms, thus offering a more serious challenge to the combined relaxation of electronic as well as nuclear degrees of freedom; (ii) delocalized orbitals play a significant role in the multicenter bonding of these molecules; and (iii) both systems represent a benchmark for the ability of LDA to treat two fascinating classes of chemical compounds, i.e., the

TABLE V. Geometrical equilibrium parameters ($d_{\text{N-H}}$ and $\theta_{\text{H-N-H}}$), dissociation energy D_e, vibrational frequencies ω_e, electrostatic dipole moment μ_e, and inversion barrier U_i, for ammonia. Experimental results are from Ref. 46; the μ_e value is from Ref. 47.

Molecule		APW	Experiment	
NH_3	$d_{\text{N-H}}$ (a.u.)	1.94	1.92	
	$\theta_{\text{H-N-H}}$	106.4°	106.5°	
	D_e (eV)	13.8	12.8	
	ω_e (cm^{-1})	3380	3337	(a_1) symmetric stretch
		980	950	(a_1) symmetric bend
		3500	3444	(e) antisymmetric stretch
		1580	1627	(e) antisymmetric bend
	μ_e (D)	1.54	1.47	
	U_i (eV)	0.19	0.25	inversion barrier

TABLE VI. Geometrical equilibrium parameters ($d_{\text{O-O}}$ and $\theta_{\text{O-O-O}}$), dissociation energy D_e, vibrational frequencies ω_e, and electrostatic dipole moment μ_e, for ozone. Geometrical experimental values are from Ref. 48; D_e from Ref. 46; ω_e from Ref. 49; μ_e from Ref. 50.

Molecule		APW	Experiment	
O_3	$d_{\text{O-O}}$ (a.u.)	2.37	2.403	
	$\theta_{\text{O-O-O}}$	117.9°	116.8°	
	D_e (eV)	7.6	1.04	
	ω_e (cm^{-1})	1200	1135	(a_1) symmetric stretch
		740	716	(a_1) bend
		1260	1089	(b_2) antisymmetric stretch
	μ_e (D)	0.64	0.53	

aromatic hydrocarbons and boron hydrides and their huge number of derivatives. In addition, these molecules can be considered as the molecular equivalents of bulk systems with extended orbitals. We can therefore expect APW results to show the same level of agreement as in bulk calculations for metals and semiconductors.[11] Finally, diborane (geometry schematically depicted in Fig. 1) represents the classic example of a molecule characterized by an electron-deficient covalent bond, where the bonding between BH_3 groups has been interpreted in terms of three-center bonds.[60] Due to the high number of atoms involved in the calculation, we did not compute vibrational properties of C_6H_6 and B_2H_6, and restricted ourselves to the determination of their molecular geometries in the present work. Table VII compares our results with experimental ones. For benzene, we did not include the C-C-C and C-C-H bond angles, which agreed with the expected value (120°). Our APW calculations were carried out using a plane-wave cutoff of 36 Ry, and a simple cubic unit cell of 15 a.u. The nonpolar character of both molecules actually permits the use of more suitable unit cells (hexagonal for C_6H_6 and tetragonal for B_2H_6), thus reducing the vacuum region within the unit cell and increasing the computational efficiency. Results obtained with different unit cells did not show significant changes in molecular geometries. The strongest disagreement with experiment, only 1.5%, occurs in the lengths of the localized C-H and B-H_t bonds. Results on benzene show an accuracy similar to those obtained in previous *ab initio* density-functional $X\alpha$ (Ref. 63) calculations[64] and *ab initio* HF optimizations.[65] In relation to diborane, our results are comparable (except for d_t) to those from HF calculations supplemented with second-order Møller-Plesset (MP) corrections to take into account electronic correlation effects.[66] From these results and the previous ones, we can conclude that the bond length between an arbitrary atom and a hydrogen atom is generally overestimated by LDA, this factor also being responsible for the small systematic deviations (lower than 1.5%) noticed in FH, H_2O, NH_3, C_6H_6, and B_2H_6. Furthermore, this deviation is more than doubled in the case of H_2 (see Table I).

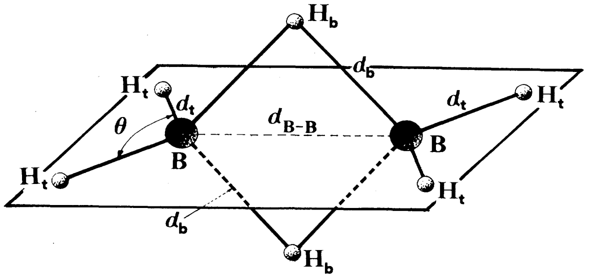

FIG. 1. A schematic representation of the diborane molecule, showing the relevant geometric parameters (see Table VII).

Having demonstrated the overall impressive results obtained for strongly bound molecules using the Soler-Williams implementation of the APW method, we applied it to different systems, namely group-IA, -IB, and -IIB dimers and hydrogen-bonded $(HF)_2$. In these dimers binding energies and vibrational frequencies are markedly smaller, and bond lengths up to three times larger than those found in diatomic or polyatomic molecules consisting of first-row atoms.

Group IA dimers have a very simple electronic structure, and show simple systematic trends with increasing atomic number. In Table VIII, we summarize our results for Li_2, Na_2, and K_2. We did not perform any calculation for the heavier alkali dimers, in which relativistic effects become important and affect equilibrium bond lengths and spectroscopic constants.[69,70] Computations were carried out using large unit cells (lattice constant of 18 a.u. for Li_2 and Na_2, and 25 a.u. for K_2), but a plane-wave energy cutoff of only 20 Ry was used. No significant changes in the equilibrium bond length were noticed when larger cutoffs were tested. Our calculated results show a reasonable agreement with experimental values. The maximum discrepancy in R_e occurs for Li_2 and Na_2,

TABLE VII. Geometrical parameters for benzene and diborane. A schematic representation of B_2H_6 is given in Fig. 1. Experimental data are from Refs. 61 (CH_6) and 62 (B_2H_6).

Molecule		APW	Experiment
C_6H_6	$d_{\text{C-C}}$ (a.u.)	2.63	2.636
	$d_{\text{C-H}}$ (a.u.)	2.08	2.048
B_2H_6	$d_{\text{B-B}}$ (a.u.)	3.30	3.345
	d_b (a.u.)	2.50	2.513
	d_t (a.u.)	2.28	2.249
	θ	121.3°	121.8°

TABLE VIII. Bond lengths R_e, dissociation energies D_e, and vibrational frequencies ω_e, for alkali dimers. Numbers in parentheses give the experimental results (Refs. 31 and 32 for Li_2; Ref. 67 for Na_2; Ref. 68 for K_2).

Dimer	R_e (a.u.)	D_e (eV)	ω_e (cm^{-1})
Li_2	5.20	1.02	322
	(5.05)	(1.03)	(351)
Na_2	5.96	0.79	157
	(5.82)	(0.75)	(159.1)
K_2	7.43	0.59	84
	(7.42)	(0.55)	(92.4)

with a relative error of 2.5%. Dissociation energies exhibit a maximum deviation of only 0.04 eV, which represents a maximum relative error of 7% in the case of K_2. The vibrational frequency ω_e must be carefully evaluated because the total-energy curve has a very shallow minimum region. This behavior is also reflected in an appreciable relative error in the calculated atomic forces, which produces an erratic motion if these forces are used in a simultaneous relaxation of both electrons and nuclei. This problem can tremendously hamper the calculations when the number of electronic degrees of freedom is increased (higher plane-wave energy cutoff). In this study of alkali dimers, we have therefore only performed a series of static computations for several fixed atomic positions. A considerable number of calculations dealing with alkali-metal dimers has already been published, and it is not the purpose of this paper to compare our results with all of them. We only mention that good agreement is obtained with previous LDA results,[33,69,71,72] and even with costly CI calculations which include core-polarization effects.[73–76]

Next, we present our APW results on group-IB and -IIB dimers, whose constituents have closed *d* shells, albeit at energies only a few eV away from valence *sp* states, and which may therefore contribute to bonding as they do in transition-metal (TM) atom clusters, which play an important role in theoretical as well as experimental research.[77–79] We have performed calculations only on four such dimers, namely Cu_2, Ag_2, Zn_2, and Cd_2. These dimers represent a stringent test for any computational scheme, since they present strikingly different properties, ranging from relatively strong binding energies in IB dimers to the very weakly bound IIB dimers. Consistently, similar differences are noticed for bond lengths and vibrational frequencies. We have excluded Au_2 and Hg_2 from this study because relativistic corrections must be included for these systems. Such corrections can be significant even for 4*d* TM dimers, leading to bond lengths contracted by almost 5% in comparison to nonrelativistic calculations.[80]

Bonding in IIB dimers has conventionally been attributed to Van der Waals interactions due to quantum charge fluctuations which are left out at the SCF level, as in the LDA or HF approximations: whereas the latter gives no indication of bonding whatsoever, the former predicts a weak covalent bond due to a slightly more pronounced *R* dependence of the energy of the σ-bonding orbital as compared to its antibonding partner which is also occupied, just as in the group-IIA dimers.[81] The successful prediction of bond lengths and binding energy trends in that series represented one of the early successes of LDA. Recently highly accurate Car-Parrinello-like pseudopotential calculations in a special basis, including *d* electrons or nonlinear core corrections, have further confirmed the power of the LDA in describing the IB and IIB dimers.[82] More recently the same approach has established that LDA with gradient corrections[9,10] yields binding energies much closer to experimental values for weakly bound systems, although their large bond lengths still tend to be underestimated.[83]

Table IX summarizes our all-electron APW results. For the sake of comparison, we also present the above-mentioned LDA pseudopotential values.[82] Large unit cells were used in our computations, especially for IIB dimers, but a plane-wave cutoff of 30 Ry was sufficient. This value was enough to obtain good convergence for the total energy, even for the problematic Cu_2 dimer. In pseudopotential calculations, a proper treatment of this dimer requires a cutoff more than ten times larger,[82] due to the unavoidable inclusion of 3*d* electrons into the valence states and the resulting deep and steep Cu pseudopotential. This serious difficulty remains in applying the pseudopotential method to TM systems. Our APW results on IB dimers agree reasonably well with experimental values and also with the above-mentioned accurate but expensive pseudopotential results; the maximum discrepancy for the overestimated binding energies amounts to 15%. As expected, calculations on IIB dimers predict drastically overestimated binding energies and much shorter bond lengths, showing the failure of LDA in describing these extremely weakly bound systems in which Van der Waals interactions can still play a role. On the other hand, agreement with pseudopotential cal-

TABLE IX. Bond lengths R_e, dissociation energies D_e, and vibrational frequencies ω_e, for IB and IIB dimers. Results obtained from APW (this work) and pseudopotential computations (Ref. 82) are compared. Experimental results are from Ref. 31 for Cu_2 and Ag_2, and Ref. 84 for Zn_2 and Cd_2.

Dimer		APW	Pseudopot.	Experiment
Cu_2	R_e (a.u.)	4.21	4.07	4.195
	D_e (eV)	2.72	3.18	1.97
	ω_e (cm^{-1})	270.2	295.1	264.5
Ag_2	R_e (a.u.)	4.84	4.69	4.67
	D_e (eV)	2.43	2.67	1.66
	ω_e (cm^{-1})	187.0	207.3	192.4
Zn_2	R_e (a.u.)	5.35	5.36	7.56
	D_e (eV)	0.23	0.22	0.06
	ω_e (cm^{-1})	85.6	83.6	(——)
Cd_2	R_e (a.u.)	6.00	5.82	9.10
	D_e (eV)	0.24	0.23	0.05
	ω_e (cm^{-1})	64.1	65.5	(——)

culations is good for all properties of IIB dimers, thus suggesting our method as a standard of accuracy for LDA-based calculations. The agreement between both calculations is only reasonable for the IB dimers, however. The remaining discrepancies merit further study.

We finish our survey with a prototype example of a hydrogen-bonded molecule. This kind of molecular bond is weakly compared with most ionic and covalent bonds, but strong in comparison with other intermolecular interactions, such as Van der Waals. Binding energies associated with this bond type range from 2 to 8 Kcal/mol and bond lengths are considerably larger than those of covalent or ionic bonds. We have performed LDA calculations on the hydrogen fluoride dimer $(FH)_2$ because this system has been extensively studied from experimental[85,86] as well as different theoretical[87–90] points of view, and its simple composition permits easier computations than those required for other thoroughly investigated systems such as $(H_2O)_2$ and $(NH_3)_2$. Due to its relatively large size and known elongate conformation, the FH dimer was placed in a simple cubic unit cell with a lattice constant of 20 a.u., and the plane-wave cutoff was 33 Ry. Calculations were carried out by relaxing electronic as well as nuclear degrees of freedom until reaching satisfactory convergence. The weak forces between the monomers resulted in a much slower convergence in comparison with that noticed for small covalent/ionic molecules.

In Fig. 2, a schematic representation of the dimer is given, showing the relevant distances and angles given in Table X. The computed F-F distance is 0.24 a.u. shorter than the experimental one,[85] this difference being larger than that obtained for typical covalent or ionic bond lengths, but smaller than the LDA underestimate found for IIB dimers. Note that the experimental binding energy[86] must be lowered by a theoretical zero-point energy,[87] as Rybak, Jeziorski, and Szalewicz[90] have pointed out. Bond angles are within the relatively large experimental error bars. In our calculation we also find that the F-H bond length of the central hydrogen atom (d_1) suffers a small expansion of 0.02 a.u. in relation to d_2. Accurate CI calculations[88] for the FH dimer reproduce the experimental geometry and dissociation energy very well, but do not show this small difference in the F-H bond lengths. However, many-body perturbation theory (MBPT) applied to this system[87] predicts a change in the d_1 distance of 0.011 a.u., closer to our result. The remaining difference between d_2 and the bond length of the monomer (see Table III) may be due to the lower plane-wave cutoff in the preset calculation, although a real change in d_2 cannot be discarded but would require a more detailed analysis. The binding energy is overestimated by only 0.11 eV, but this represents a relative error of 50%, illustrating again this well-known deficiency of the LDA. Our comparison shows that the LDA representation of the hydrogen bond is midway between the remarkable representation of both covalent and ionic bonds and the inadequate description of weak bonds such as those in IIB dimers.

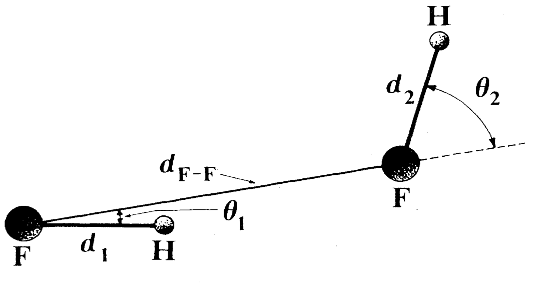

FIG. 2. A schematic representation of the hydrogen-bonded FH · · · FH dimer, showing the relevant geometric parameters (see Table X).

TABLE X. Equilibrium geometry (bond lengths and angles) and dimer binding energy D_e for hydrogen-bonded FH · · · FH. Geometrical parameters are schematically presented in Fig. 2. Experimental results are from Ref. 85; the dimer binding energy from Ref. 86 has been corrected by a theoretical estimate of the zero-point energy (Ref. 87).

Molecule		APW	Experiment
FH · · · FH	$d_{\text{F-F}}$ (a.u.)	4.90	5.14±0.06
	d_1 (a.u.)	1.80	(——)
	d_2 (a.u.)	1.78	(——)
	θ_1	4.3°	10±6°
	θ_2	68.9°	63±6°
	D_e (eV)	0.32	0.21

IV. CONCLUSIONS

We have presented accurate LDA-based calculations on a wide variety of small molecules, using the Soler-Williams implementation of the APW method in a supercell computational scheme. In view of its all-electron nature, versatility, and superior accuracy, this scheme provides a benchmark for testing the performance of the LDA, essentially free of any uncontrolled ambiguities due to basis set inadequacy or pseudopotential fits. The ability to compute atomic forces directly and accurately has been further tested, and permitted a simultaneous adjustment of both electronic and nuclear degrees of freedom, in the self-consistent iterative procedure. Good results are obtained for equilibrium properties of small diatomic and polyatomic molecules made of first-row atoms, showing a maximum deviation of 2% for bond lengths and bond angles, although binding energies are systematically overestimated, especially when the bonding is primarily covalent and (nearly) degenerate electronic configurations compete, thus enhancing the importance of correlation effects. However, at this point, we must comment that this deficiency in the evaluation of binding energies has been already corrected by including gradients corrections (GC) to the simpler LDA,[33,43,91] diminishing errors up to values featuring other more demanding techniques. Dipole moments are obtained with an accuracy of 0.1 D and vibrational frequencies with an average deviation of 40 cm^{-1}, although for most diatomic molecules the precision achieved is even higher. The same scheme has been applied to group-IA, -IB, and -IIB dimers as well as hydrogen-bound $(HF)_2$, revealing in addition seriously underestimated bond lengths and overestimated vibrational frequencies for the very weakly bound IIB dimers, but reasonable values for the others, even for binding energies in the case of alkali dimers. Furthermore, comparisons with recent accurate pseudopotential calculations on IA and IIB dimers with a special symmetry-adapted basis set[82] indicate the quality of our more versatile APW scheme as a LDA benchmark. Taken as a whole, our results show that several important properties of molecules exemplifying bonds of different kinds and strengths at and near equilibrium are well reproduced by our scheme, although weakly bound systems reveal systematic deviations. Our APW scheme also opens the possibility of studying more complex molecules which incorporate transition-metal atoms, e.g., clusters and carbonyls, as well as clean and adsorbate-covered TM surfaces and defects, including relaxation of neighboring atoms. We would stress that in all cases the code is exactly the same as that used for bulk or surface calculations, without special modifications, giving our computational tool an enormous flexibility in applications to different problems.

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*Present address: Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

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