Optimized Gaussian exponents for Goedecker-Teter-Hutter pseudopotentials

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We have optimized the exponents of Gaussian s and p basis functions for the elements H, B–F, and Al–Cl using the pseudopotentials of Goedecker, Teter, and Hutter [Phys. Rev. B 54, 1703 (1996)] by minimizing the total energy of dimers. We found that this procedure causes the Gaussian to be somewhat more localized than the usual procedure, where the exponents are optimized for atoms. We further found that three exponents, equal for s and p orbitals, are sufficient to reasonably describe the electronic structure of all elements that we have studied. For Li and Be results are presented for pseudopotentials of Hartwigsen et al. [Phys. Rev. B 58, 3641 (1998)]. We expect that our exponents will be useful for density functional theory studies where speed is important.

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I. INTRODUCTION

Density functional theory1,2 (DFT) has become a standard tool for electronic structure calculations in condensed-matter physics. Using computer clusters, nowadays even solids with several hundreds of atoms per unit cell can routinely be studied. For molecular dynamics simulations of large systems, however, existing codes are still too slow to be able to perform large numbers of time steps within a reasonable amount of time. To overcome this problem, faster DFT codes are needed. To this purpose two approximations are very useful. First of all, pseudopotentials eliminate the need to take into account core electrons and simplify the computation for the valence electrons by being softer than the original all-electron potentials, thus reducing the number of basis functions that have to be included in practical calculations. Secondly, the use of localized (atom-centered) basis states makes it possible to compute many quantities, such as, the electronic density, by means of procedures that scale linearly with the number of atoms in the unit cell [so-called order(N) methods]. Unfortunately, although many different pseudopotentials have been published throughout the years, the problem of finding the best possible local basis functions for these pseudopotentials is only rarely addressed. One reason is that the form of such optimized basis states depends on the pseudopotentials used and is thus not universal. Another reason is perhaps that local basis states, especially Gaussians, are mainly used by quantum chemists, who are often interested in getting the most accurate results possible, which arguably speaks against approximating the all-electron potential by pseudopotentials. We would here like to stress that our goal is to perform calculations on large systems, trading accuracy for speed, and to compete with tight-binding methods predominantly used for such systems.2,5

Toward our proposed goal we present, in this paper, optimized Gaussian exponents for the pseudopotentials of Goedecker, Teter, and Hutter.2 We chose Gaussians as basis functions in part because a lot of literature exists that describes how to calculate Hamiltonian matrix elements in an efficient, analytical way, and in part because the tails of Gaussian functions decay very rapidly. The latter property can be exploited to speed up the ensuing computer code. We have selected the pseudopotentials of Goedecker, Teter, and Hutter,2 for the following reasons: (1) They have an analytical form, which is characterized by only a few parameters. (2) Their form has been optimized for efficient real-space DFT computations. (3) They are available for the first two rows of the periodic table. (4) Pseudopotentials of a slightly generalized form are available for elements throughout the periodic table [See Hartwigsen et al. (Ref. 7)]. (5) Their validity has been thoroughly tested,2 among other ways by comparing bond lengths of 34 small molecules with all-electron DFT results. (6) They can be used in ABINIT,8 a freely available DFT program, which uses a plane wave basis. We used ABINIT to obtain highly accurate reference results for dimers of the elements that we studied as well as for a number of other small molecules. The remainder of this paper is organized as follows. In Sec. II we describe our DFT calculations. Our optimized exponents are presented in Sec. III. We conclude in Sec. IV.

II. COMPUTATIONAL PROCEDURE

For our DFT calculations we wrote a program following the work of Obara and Saika9 which gives recursive expressions for overlap, kinetic, and Hartree matrix elements of s- and p-type orbitals, starting from the much easier expressions for s-type orbitals. Corresponding expressions for the Goedecker-Teter-Hutter pseudopotentials were straightforwardly derived. The exchange and correlation potential (we used the local density approximation of Perdew and Wang10) was calculated on a fine mesh of grid points, without further approximations. For the Hartree matrix elements the exact four-center integrals were calculated. No intermediate fitting procedure was used for the charge density. In the selfconsistent loop the density matrix, describing the electronic charge density, was mixed using Broyden mixing.11 Electronic occupation numbers were calculated according to the Fermi-Dirac statistics with an electronic temperature of 1 mK. Because our main interest is in optimizing exponents for speed, we limited ourselves to Gaussian basis states with s and p character only, an approximation which should work best for light elements.
As mentioned above, reference results were obtained with the computer program ABINIT. This program uses periodic boundary conditions and a plane wave basis. For the ABINIT results presented below, a careful convergence study was made with respect to the box size and the number of plane waves included to ensure that the total free energies obtained were converged to within 1 mHa or better.

III. RESULTS

Usually Gaussian exponents are optimized for atoms, which may not give optimal results for molecules or solids. To improve on this situation we used dimers for our optimizations. We found that the Gaussian functions became somewhat more localized as compared to the atomic optimizations, which is favorable if speed is important (fewer matrix elements need to be calculated). For Si we additionally optimized the exponents for three atoms arranged on the corners of a triangle and for four atoms located on the vertices of a square. For these latter optimizations we found no systematic change in the exponents. Therefore, we decided to optimize our Gaussian basis functions using dimers.

In our optimization procedure the total free energy of the dimers was minimized including different numbers of $s$ and $p$ orbitals in the basis. The following configurations were tested: $1sp$, $1s1p$, $1s2p$, $2sp$, $2s1p$, $2s2p$, $2s3p$, $3sp$, $3s1p$, $3s2p$, $3s3p$, $4sp$, $4s3p$, $4s4p$, where $nsmp$ means that $n$ $s$-type and $m$ $p$-type Gaussians were used, and $ns$ indicates that every one of $n$ exponents were used for $s$ and $p$ Gaussians. The possibility of equal $s$- and $p$-exponents was included, because it is computationally advantageous (see, for example, Ref. 9). After each optimization, we computed the binding energy of the dimer for a wide range of atomic separations.

Surprisingly, we found that the $3sp$ data gave close to optimal results for the binding energies of all dimers. The resulting curves are shown in Figs. 1 and 2. For hydrogen, the $4sp$ curve (not shown) was slightly better than the $3sp$ curve, but the energy differences between both curves were small compared to the errors that we made in other elements by restricting ourselves to a basis containing only $s$ and $p$ orbitals. For lithium and beryllium the pseudopotentials of Goedecker, Teter, and Hutter treat the $1s$ electrons as valence electrons, and offer therefore only a limited advantage in speed as compared to all-electron calculations. For this reason, for these two elements we decided to use the above-mentioned pseudopotentials of Hartwigsen et al., which for Li and Be happen to be parameterized by the same analytical form as the pseudopotentials of Goedecker, Teter, and Hutter, so that no additional programming was necessary for these elements. The Li and Be pseudopotentials of Hartwigsen et al. have that we have used treat the $1s$ electrons as core electrons, and should thus provide a considerable speed-up as compared to all-electron calculations.

As one can see in Fig. 1, our results for H, Li, Be, B, and C are excellent. At first sight, the agreement of our dimer curve with the corresponding ABINIT reference curve looks slightly worse for Be$_2$ [Fig. 1(c)] than for the other dimers [Figs. 1(a), 1(b), 1(d), and 1(e)]. The reason is that the binding energy of Be$_2$ at its equilibrium distance is approximatively an order of magnitude less than that of, for example, H$_2$ or C$_2$. As a result, the $3p$ basis set errors look large for Be$_2$ [Fig. 1(c)], even though the absolute error is less than 9 mHa for all distances shown (2.5 mHa at the minimum), which should be acceptable for most applications. In Fig. 1 starting from nitrogen, the incompleteness of our basis set becomes gradually noticed, and as a result the agreement between our results and the ABINIT reference curves becomes gradually worse. The same behavior can be noticed in the dimer curves for the second-row elements, which are shown in Fig. 2. Whereas the $3sp$ basis set gives very reasonable results for Al, Si, and P, the curves for sulphur and chlorine differ increasingly from the ABINIT reference curves. It would, of course, depend on the application, whether the deviations are acceptable. For future reference, all our optimized $3sp$ exponents for H, Li–F, and Al–Cl are presented in Table 1.

Table I: Optimized Gaussian basis set exponents for H, Li–F, and Al–Cl. The same exponents should be used for Gaussian $s$ and $p$ orbitals. The second column gives the atomic separations ($d$) of the dimers for which the exponents were optimized. It should be stressed that we have made with respect to the box size and the number of plane waves included to ensure that the total free energies obtained were converged to within 1 mHa or better.

| Molecule | Bond Length ($a_0$) | Binding Energy (Ha) |
|----------|--------------------|---------------------|
|          | 3sp data | ABINIT | 3sp data | ABINIT |
| BH       | 2.383    | 2.366  | −0.180   | −0.1857 |
| FH       | 1.784    | 1.763  | −0.2970  | −0.3026 |
| AlH      | 3.210    | 3.161  | −0.1573  | −0.1599 |
| AlCl     | 2.451    | 2.435  | −0.2212  | −0.2279 |
| CO       | 2.162    | 2.127  | −0.5322  | −0.5715 |
| CS       | 3.003    | 2.884  | −0.3422  | −0.3912 |
| PN       | 2.930    | 2.789  | −0.3978  | −0.4528 |
| SiO      | 2.977    | 2.833  | −0.3854  | −0.4368 |

Table II: Bond lengths and binding energies of diatomic molecules obtained using the $3sp$ Gaussian basis sets from Table 1. Reference results were calculated using the computer program ABINIT.
FIG. 1: (Color online) The binding energy as a function of atomic distance for the dimers (a) H$_2$ and (b)–(h) Li$_2$–F$_2$. The curves labeled ABINIT show reference results obtained with the computer program ABINIT. The curves labeled “3sp data” show the results that we have obtained using optimized basis sets with 3 different exponents, but identical for s and p Gaussians. It should be stressed that the results for (b) Li and (c) Be were obtained using pseudopotentials of Hartwigsen et al., whereas all other curves were calculated using Goedecker-Teter-Hutter pseudopotentials.
first thing to be noticed is that the bond lengths obtained with the Gaussian 3sp basis sets are always larger than the ABINIT reference bond lengths, which are also given in Table III and that the 3sp binding energies are always smaller than the reference results, with the exception of BH, for which the 3sp and the reference binding energies agree almost perfectly. These trends are consistent with what can be observed for the dimers (Figs. 1 and 2). A more quantitative analysis shows that for BH, FH, AlH, HCl, and CO the Gaussian 3sp basis reproduces the ABINIT bond lengths to within 2%, and that for CS, PN, and SiO the deviations of the bond lengths are of the order of 5%. The errors in the binding energies are between 0.3 and 6.7 mHa for BH, FH, AlH, and ClH, and between 39.3 and 55 mHa for CO, CS, PN, and SiO, but never more than 12.5% of the ABINIT reference binding energy. All these errors lie within the range of what one might reasonably have expected from the dimer curves (Figs. 1 and 2), and we conclude that our Gaussian 3sp basis sets perform equally well for the dimers and the small molecules that we have studied. We once again remind the reader that our main goal in the present work is to compete with tight-binding theory rather than to produce very accurate results for a variety of small molecules composed of first and second row elements.
IV. CONCLUSION

In this paper we have optimized Gaussian exponents for the Goedecker-Teter-Hutter pseudopotentials\(^6\) for all elements in the first two rows of the periodic table, with the exception of the noble gases and Na and Mg. We decided not to include the noble gases in our study, because the local density approximation\(^10\) is known to perform quite badly for these elements. Sodium and magnesium were kept out of the scope of this study, because the Goedecker-Teter-Hutter pseudopotentials\(^6\) treat the 2s and 2p electrons as valence electrons, which would make practical applications unnecessarily expensive in terms of computer time.

The main conclusion of the present work is that for all elements studied it is sufficient to use a Gaussian basis containing only s and p orbitals, and furthermore that only three Gaussian exponents, which can be chosen equal for the s and the p channels, are needed to obtain a reasonable accuracy, as has been discussed in the body of this paper.

We believe that our results constitute an important contribution towards the development of fast DFT computer programs using both pseudopotentials and Gaussian basis sets.

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