Ground and Excited State Density Functional Calculations with the Gaussian and Augmented-Plane-Wave Method

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Abstract: The calculation of the electronic structure of large systems by methods based on density functional theory has recently gained a central role in molecular simulations. However, the extensive study of quantities like excited states and related properties is still out of reach due to high computational costs. We present a new implementation of a hybrid method, the Gaussian and Augmented-Plane-Wave (GAPW) method, where the electronic density is partitioned in hard and soft contributions. The former are local terms naturally expanded in a Gaussian basis, whereas the soft contributions are expanded in plane-waves by using a low energy cutoff, without loss in accuracy, even for all-electron calculations. For the calculation of excitation energies a recently developed, time-dependent density functional response theory (TD-DFRT) technique is joined with the GAPW procedure. We demonstrate the accuracy of the method by comparison with standard quantum chemistry calculations for a set of small molecules. To highlight the performance and efficiency of GAPW we show calculations on systems with several thousands of basis functions.

Keywords: Computational chemistry · Condensed systems · Density functional theory · Plane waves

Introduction

Density functional theory (DFT) [1] is the method of choice for the calculation of electronic properties of large systems. This is due to the combination of accuracy and efficiency that has been achieved for the Kohn-Sham (KS) method in DFT [2]. The success of the KS method makes it also the primary target for new developments to increase both accuracy and efficiency. Increase in accuracy has to be achieved in two fields. On one hand the numerical limit of a given model (*i.e.* exchange-correlation functional

in DFT) should be reached and on the other hand more accurate models should be developed. The development of new functionals is an art on its own and will not concern us here. However, it is intimately related to the efficiency problem, as only numerically accurate tests on more and more complex systems can give unambiguous information on the performance of new functionals. The goal of improved algorithms is therefore, to provide methods to accurately and efficiently solve the KS equations.

Our recent work has focused on the development of methods to perform KS calculations using accurate basis sets on large systems, including condensed matter systems requiring periodic boundary conditions (PBC). The methods are based on a dual approach [3][4], where the KS orbitals are expanded in Gaussian type basis sets, common in most standard quantum chemistry codes, and the electronic charge density is represented using a plane-wave (PW) basis. In this basis the calculation of the *Hartree* potential is straightforward and by making use of fast Fourier transforms (FFT) the complexity of this part of the calculation becomes $O(N \log N)$, where N is the number of basis functions taken as a measure of the system size [3][4]. In order to reduce the size of the PW basis set pseudopotentials (PP) of the dual-space type [5][6] are used. The latest implementation of the Gauss-

ian and plane-wave (GPW) method [4] has been done within the CP2K program and the corresponding module is called Quickstep [7]. In this implementation the linear scaling calculation of the GPW KS matrix elements is combined with an optimizer based on orbital transformations [8]. This optimization algorithm scales linearly in the number of basis functions for a given system size and, in combination with parallel computers, it can be used for systems with several thousands of basis functions.

The GPW method is very efficient in comparison with other methods. However, since we rely on the PP approximation in order to limit the size of the PW basis, GPW is not suited for all those applications that require the full electron density. Moreover, even when PP are used, systems containing second-row transition metals require the inclusion of rather localized semi-core states into the valence region. The resulting density can be properly described with a PW expansion only using a very large basis set, therefore reducing the efficiency of the GPW method. These drawbacks of the GPW method have been overcome with the Gaussian and augmented-plane-wave (GAPW) method [10][11]. The GAPW method uses the PW representation of the density only for the smoothly varying density between atoms, but relies on localized functions for the rapidly varying density close to the nu-

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clei. The basic idea of this separation was taken from the projector augmented-wave (PAW) scheme proposed by Blöchl [12]. Here we report on the implementation of the GAPW scheme in the Quickstep code. Accuracy and performance data are shown. The GAPW method for ground state DFT calculations is extended to linear response within time-dependent DFT. First tests of the implementation show a satisfying accuracy and open promising perspectives for the calculation of the excitation energies in extended systems.

GAPW Method

Like many other approaches in quantum chemistry, the GAPW method uses a basis of contracted Gaussian functions to expand the Kohn-Sham orbitals $\phi_i(\mathbf{r})$

$$\phi_i(\mathbf{r}) = \sum_{\alpha} C_{\alpha i} \varphi_{\alpha}(\mathbf{r}) \quad ,$$
$$\varphi_{\alpha}(\mathbf{r}) = \sum_{m} d_{m\alpha} g_m(\mathbf{r}) \tag{1}$$

The contraction coefficients $d_{m\alpha}$ are held fixed during a calculation and the functions $g_m(\mathbf{r})$ are primitive Gaussian functions characterized by the order of their monomial pre-factor and their exponent α_m

$$g_m(r) = x^{l_x} y^{l_y} z^{l_z} e^{-\alpha_m r^2} \tag{2}$$

These simple functions are the natural basis set to describe atomic and molecular orbitals. Furthermore all the density independent contributions to the KS Hamiltonian, like the kinetic energy and the electronic interaction with the ionic cores, can be calculated analytically using integral recurrence relations [13]. In order to avoid the cumbersome and time-consuming four center integrals needed for the Coulomb terms, the GPW method exploits the PW representation of the density. The Coulomb potential is then calculated in reciprocal space using fast Fourier transforms [3]. However, the PW basis set is not appropriate to describe the complex structure of the electronic density in the vicinity of the atoms. For this reason the GAPW method uses a dual representation of the electronic density, where the usual expansion of the density using the density matrix P

$$n(r) = \sum_{\alpha\beta} P_{\alpha\beta} \varphi_{\alpha}(r) \varphi_{\beta}^*(r) \tag{3}$$

is replaced in the calculation of the Coulomb and exchange-correlation (xc) energy by

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \sum_A \tilde{n}_A(\mathbf{r}) \tag{4}$$

In our current implementation the densities $\tilde{n}(\mathbf{r})$, $n_A(\mathbf{r})$, and $\tilde{n}_A(\mathbf{r})$ are expanded in plane-waves and products of primitive Gaussians centered on atom A, respectively

$$\tilde{n}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$
$$n_A(\mathbf{r}) = \sum_{mn \in A} P_{mn}^A g_m(\mathbf{r}) g_n^*(\mathbf{r}),$$
$$\tilde{n}_A(\mathbf{r}) = \sum_{mn \in A} \tilde{P}_{mn}^A g_m(\mathbf{r}) g_n^*(\mathbf{r}) \tag{5}$$

In Eqn. (5), $\tilde{n}(\mathbf{G})$ are the Fourier coefficients of the soft density, as obtained from Eqn. (3) by keeping in the expansion of the contracted Gaussians only the primitives with exponents smaller than a given threshold. Ω denotes the volume of the periodic cell and all wave-vectors $\mathbf{G}$ corresponding to a given grid spacing are included in the expansion. The expansion coefficients P_{mn}^A, and $\tilde{P}_{mn}^A$ are also functions of the density matrix $P_{\alpha\beta}$ and can be calculated efficiently [11].

The separation of the density from Eqn. (5) is borrowed from the projector augmented-wave approach [12]. Its special form allows the separation of the smooth parts, characteristic of the interatomic regions, from the quickly varying parts close to the atoms, while still expanding integrals over all space. The sum of the contributions in Eqn. (3) gives the correct full density if the following conditions are fulfilled

$$\begin{array}{llll} n(\mathbf{r}) = n_A(\mathbf{r}) & \tilde{n}(\mathbf{r}) = \tilde{n}_A(\mathbf{r}) & \textit{close to atom } A \\ n(\mathbf{r}) = \tilde{n}(\mathbf{r}) & n_A(\mathbf{r}) = \tilde{n}_A(\mathbf{r}) & \textit{far from atom } A \end{array} \tag{6}$$

The first conditions are exactly satisfied only in the limit of a complete basis set. However, the approximation introduced in the construction of the local densities can be systematically improved by choosing larger basis sets.

For semi-local xc functionals such as the local density approximation, general gradient approximations or meta functionals using the kinetic energy density, the xc energy can be simply written as

$$E_{xc}^{GAPW}[n] = E_{xc}[\tilde{n}] + \sum_A E_{xc}[n_A] - \sum_A E_{xc}[\tilde{n}_A] \tag{7}$$

The first term is calculated on the real-space grid defined by the plane-wave ex-

pansion and the other two are efficiently and accurately calculated using atom centered meshes.

Due to the non-local character of the Coulomb operator, the decomposition for the electrostatic energy is more complex. In order to distinguish between local and global terms, we need to introduce atom-dependent screening densities, n_A^0 (hard) and $\tilde{n}_A^0$ (soft), that generate the same multipole expansion Q_A^{lm} as the local density $n_A - \tilde{n}_A + n_A^Z$, where n_A^Z is the nuclear charge of atom A.

$$n_A^0(\mathbf{r}) = \sum_{lm} Q_A^{lm} g_A^{lm}(\mathbf{r}),$$
$$\tilde{n}_A^0(\mathbf{r}) = \sum_{lm} Q_A^{lm} \tilde{g}_A^{lm}(\mathbf{r}) \tag{8}$$

The primitive Gaussian $g_A^{lm}(\mathbf{r})$ and $\tilde{g}_A^{lm}(\mathbf{r})$ are defined with large and small exponents, respectively, and normalized. Since the sum of local densities $n_A - \tilde{n}_A + n_A^Z - n_A^0$ has vanishing multiple moments, it does not interact with charges outside the localization region, and the corresponding energy contribution can be calculated by one-center integrals. The final form of the Coulomb energy in the GAPW method reads [11] then

$$E_H^{GAPW}[n + n^Z] = E_H[\tilde{n} + \tilde{n}^0] +$$
$$E_H[n^0] - E_H[\tilde{n}^0] +$$
$$\int d\mathbf{r} V_H(n^0(\mathbf{r}) - \tilde{n}^0(\mathbf{r})) \tilde{n}(\mathbf{r}) +$$
$$\sum_A E_H[n_A + n_A^Z] - \sum_A E_H[\tilde{n}_A + n_A^0] \tag{9}$$

where quantities n^0, $\tilde{n}^0$ are summed over all atomic contributions, and $E_H[n]$ and $V_H(n(\mathbf{r}))$ denote Coulomb energy and potential of a charge distribution n. The first term in Eqn. (9) can be calculated efficiently using fast Fourier transform methods. The next three terms involve Coulomb integrals over two and three Gaussian functions. The special form of these terms allow them to be calculated efficiently using analytic integral formulas [13]. The final terms are one-centered and are calculated in our current implementation on radial atomic grids.

The total electronic energy within the GAPW method is therefore calculated from

$$E_{el} = \sum_{\alpha\beta} P_{\alpha\beta} h_{\alpha\beta} + E_H^{GAPW}[n + n^z] + E_{xc}^{GAPW}[n] \tag{10}$$

where $h_{\alpha\beta}$ denotes matrix elements of the core Hamiltonian, the sum of kinetic energy and local part of the external potential [10][11]. The special form of the GAPW

energy functional involves several approximations in addition to a standard implementation. The number of reciprocal space vectors included in the expansion of the smooth density $\tilde{n}(\mathbf{r})$ controls the accuracy of the corresponding terms in Coulomb and xc energy. The accuracy of the local expansion of the density is controlled by the flexibility of the product basis of primitive Gaussians. As we fix this basis to the primitive Gaussians present in the original basis we cannot independently vary the accuracy of the expansion. Therefore, we have to consider this approximation as inherent to the primary basis used.

Time-dependent DFT with GAPW

Excitation energies in time-dependent DFT (TDDFT) are defined as the stationary points of the functional [14][15]

$$G[x, y, z] = \frac{1}{2}\left(x^{\dagger}(A + B)x + y^{\dagger}(A + B)y\right) + \frac{w}{2}\left(x^{\dagger}y + y^{\dagger}x - 2\right) \quad (11)$$

The Lagrange multiplier w is real valued and is in the adiabatic approximation equal to the excitation energy ω at the stationary points. The first order response of the one-particle density matrix $P^{(1)}(\mathbf{r}, \mathbf{r'})$ is related to the vectors x and y

$$P^{(1)}(\mathbf{r}, \mathbf{r'}) = \frac{1}{2}\sum_{ia\sigma}\left((x_{ia\sigma} + y_{ia\sigma})\Phi_{i\sigma}(\mathbf{r})\Phi_{a\sigma}(\mathbf{r'}) + (x_{ia\sigma} - y_{ia\sigma})\Phi_{i\sigma}(\mathbf{r'})\Phi_{a\sigma}(\mathbf{r})\right) \quad (12)$$

The sums extend over all occupied states i and unoccupied states a of spin symmetry σ and $\Phi_{i\sigma}(\mathbf{r})$ are optimized Kohn-Sham orbitals. The matrices A and B are defined by

$$A_{ia\sigma, jb\sigma'} = \left(F_{ab\sigma}\delta_{ij} - F_{ij\sigma'}\delta_{ab}\right)\delta_{\sigma\sigma'} + B_{ia\sigma, jb\sigma'}$$

$$B_{ia\sigma, jb\sigma'} = \left\langle ia\sigma \mid f_{Hxc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r'}) \mid jb\sigma'\right\rangle \quad (13)$$

In this Eqn. $F_{ab\sigma}$ denotes the KS matrix in the basis of KS orbitals $\Phi_{a\sigma}(\mathbf{r})$ and $f_{Hxc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r'})$ denotes the kernel function evaluated at the ground state density

$$f_{Hxc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r'}) = \frac{1}{\mathbf{r} - \mathbf{r'}} + \frac{\delta^2 E_{xc}}{\delta n_{\sigma}\delta n_{\sigma'}} \quad (14)$$

In our implementation we make use of the Tamm-Dancoff approximation [15] that is most easily recovered by setting $x = -y$ in Eqn. (11)

$$G[x, w] = x^{\dagger}(A + B)x - w(x^{\dagger}x - 1) \quad (15)$$

To obtain working expressions for the operators within the GAPW method we replace the Kohn-Sham matrix F by its GAPW formulation and write the contribution of the kernel function to the energy functional G as

$$\langle x \mid f_{Hxc} \mid x \rangle = E_H\left[n^{(1)}\right] + \int d\mathbf{r}\ f(\mathbf{r})n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r}) \quad (16)$$

where $n^{(1)}(\mathbf{r}) = 2\sum_{ia\sigma} x_{ia\sigma}\Phi_{i\sigma}(\mathbf{r})\Phi_{a\sigma}(\mathbf{r})$ and the xc kernel is derived from a semi-local xc functional. By a straightforward extension of the GAPW charge density decomposition to the response density

$$n^{(1)}(\mathbf{r}) = \tilde{n}^{(1)}(\mathbf{r}) + \sum_A n_A^{(1)}(\mathbf{r}) - \sum_A \tilde{n}_A^{(1)}(\mathbf{r}) \quad (17)$$

we find

$$\langle x \mid f_{Hxc} \mid x \rangle = E_H^{GAPW}\left[n^{(1)}\right] + f_{xc}\left[\tilde{n}^{(1)}\right] + \sum_A f_{xc}\left[n_A^{(1)}\right] - \sum_A f_{xc}\left[\tilde{n}_A^{(1)}\right] \quad (18)$$

The functions $f_{xc}[n]$ denote integrals of the type

$$f_{xc}[n] = \int d\mathbf{r}\ f(\mathbf{r})n(\mathbf{r})n(\mathbf{r}) \quad (19)$$

Accuracy

To assess the accuracy of the GAPW method we compare molecular structures and total energies of a series of small molecules with results obtained by standard quantum chemistry packages [16][17] for the BLYP density functional [18][19]. The results from the standard calculations can be considered the limiting values of a GAPW calculation that have to be reached for the case of a complete plane-wave and local function basis. The maximum error in bond length for the set of tested molecules is shown in Fig. 1. The calculations were performed with a *6-31G** and *6-311++G(3df,3dp)* Gaussian basis sets. The error is for all cases below 0.2 pm.

The plane-wave basis can be improved independently and the test calculations have been performed with a kinetic energy cutoff of 250 Ry. This value ensures almost converged results for the plane-wave part. The expansion of the local atomic densities relies on the primitive Gaussians present in the primary basis set. We therefore can expect that large basis sets will have results closer to the reference value. This is confirmed by the decrease in the maximum difference in the bond length reported for almost all the molecules that have been optimized also with the large basis set. This feature is even more evident from the differences in the single point energies and the energies of the optimized structures, which can be seen in Fig. 2. While for the smaller basis set the energy differences are always lower than 1 *mHartree*, with the 6-311++G(3df,3dp) ba-
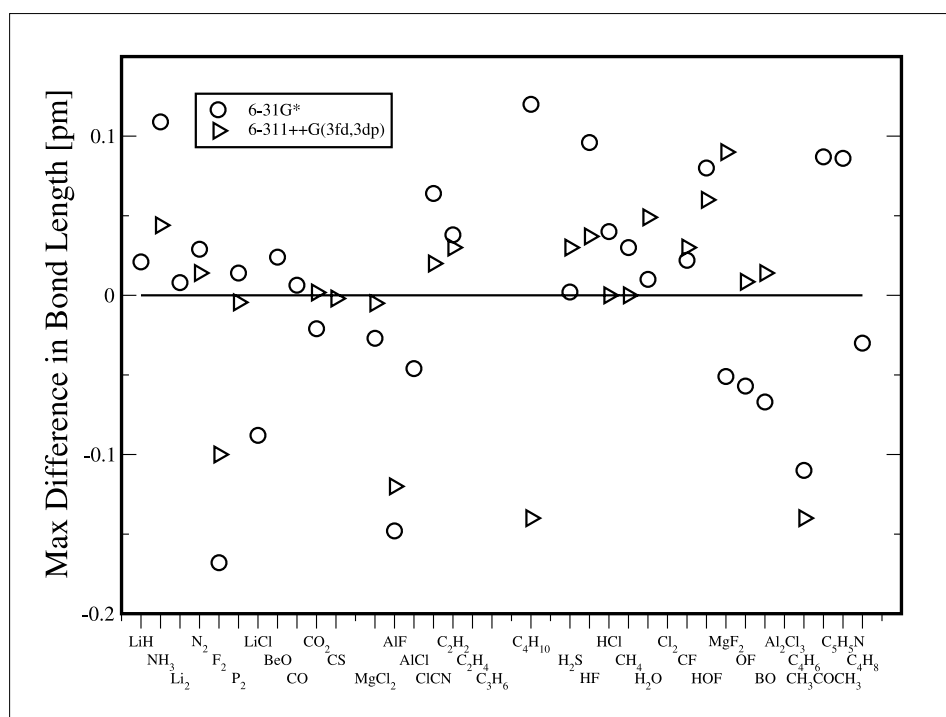

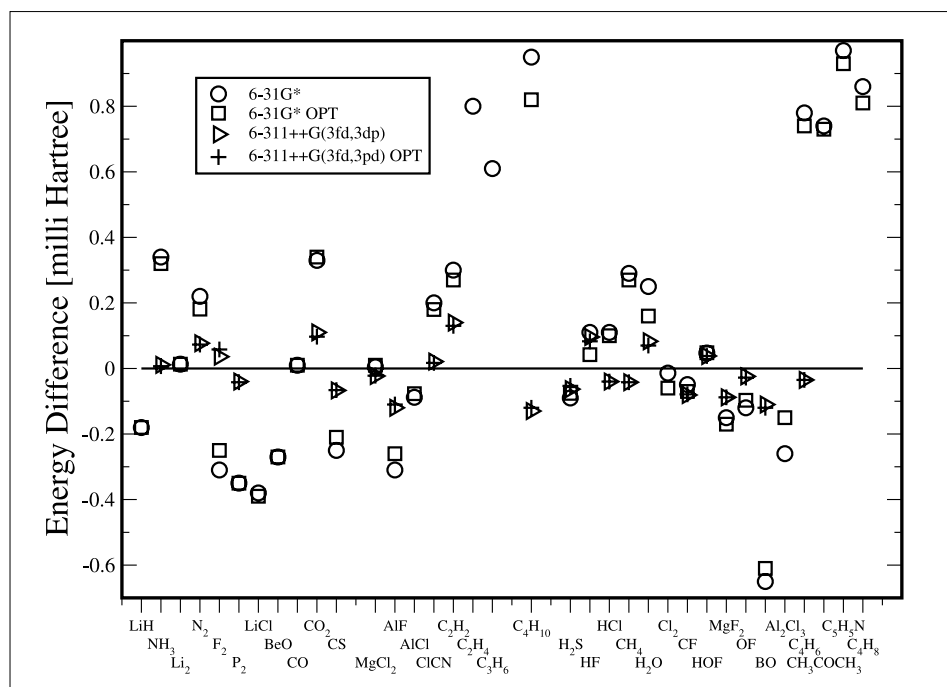Fig. 1. Difference in bond length [pm] of a set of small molecules for two basis sets

Fig. 2. Difference in total energy [mHartree] for a set of small energies. Calculations are performed for two basis sets at experimental and optimized geometries

sis they decrease to values below 0.1 *mHartree*. This number has to be compared with difference of the same order or larger for auxiliary basis calculations [20].

As expected, the GAPW method shows a faster convergence with the PW energy cutoff than the GPW method. We performed a set of geometry optimizations for a water molecule in a cubic box of 15 Å, with the BLYP functional, dual-space PP [5] and energy cutoff ranging from 100 to 1000 Ry. We observe that already at 200 Ry the total energy is converged within ~1 μE_h and the bond lengths fluctuations are below 20 μÅ. Without adding any smoothing correction, the GPW method can reach such stability only for energy cutoff above 800 Ry [4].

Calculation methods that involve regular grids or plane-wave basis sets for the evaluation of the exchange and correlation integrals all show a periodic dependence of the total energy on the grid spacing. These energy ripples are also known in plane-wave basis calculations and are often very irritating, especially for high precision calculations. In the GPW method the ripples problem is enhanced by a special property of the pseudopotentials employed. The dual-space pseudopotentials produce atomic densities that approach a zero value at the nuclei and it has been shown that this can lead to numerical problems. However, in the GAPW method this problem is largely avoided by the construction of the smooth density that is used in the plane-wave expansion. The effect of this smoothing is easily seen in Fig. 3 where the d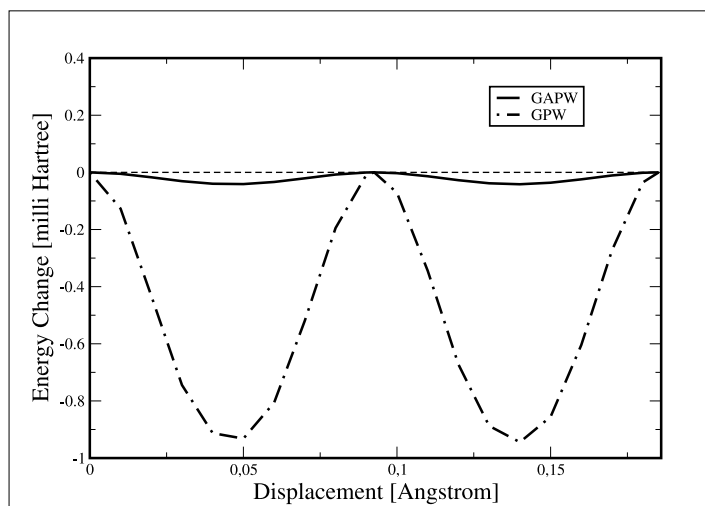ependence of the total energy on the grid position is shown for both a GPW and GAPW calculation of a single water molecule. The maximum change of the total energy is reduced in the GAPW method by more than an order of magnitude using the same plane-wave cutoff of 300 Ry.

Finally, we performed a series of calculations on low-lying excited states of water and formaldehyde. Results from the GAPW implementation of TDDFT compare well with the corresponding results from standard quantum chemistry codes [16][17] (see Table). The calculations have been performed using the PBE functional [21] with a quadruple-zeta valence type basis augmented with diffuse functions and three sets of polarization functions and dual-space pseudopotentials [5] for formaldehyde. The standard quantum chemistry calculations used an *aug-cc-pVQZ* basis for both molecules and the same basis was used in an all-electron GAPW calculation for water. Remaining differences can be attributed to the use of pseudopotentials in one of the calculations, the approximations from the GAPW method and the use of the Tamm-Dancoff approximation.

Performance

The performance of the current implementation of the GAPW method has been tested with two types of systems. Both calculations employ the BLYP functional [18][19] and a 200 Ry plane-wave cutoff. A series of calculations on water with increasing system size shows the overall actual scaling of the method. In Fig. 4 the CPU times for a single SCF iteration for water systems from 32 to 1024 molecules are shown. One series of calculations has been performed with a triple zeta valence basis set with two polarization functions and pseudopotentials, leading to 40 basis functions per molecule. The other series uses the all-electron implementation of GAPW and a triple zeta valence basis set with a single set of polarization functions, leading to 30 basis functions per molecule. The two largest calculations are therefore a pseudopotential calculation with 3072 atoms, resulting in 4096 occupied orbitals expanded in 40'960 basis functions and an all-electron calculation of 512 water molecules with 2560 occupied KS states expanded in 15'360 basis functions. The water test calculations were run on an IBM p690 computer with 32 CPUs. By the use of efficient screening procedures, we exploit the sparsity of the KS Hamiltonian, which couples only basis functions that are located on nearby atoms. The construction of the KS matrix and of the density scales, therefore, linearly with the size of the system. The slight deviation from linear behavior for the large systems that can be seen in Fig. 4 is due to the operations on molecular orbitals that have to be

Fig. 3. Change in energy for a single water molecule as a function of position

Table. Excitation energies [eV] as calculated from TD-DFRT. Excitations are labelled as R for Rydberg and V for Valence

Molecule	Symmetry	GAPW	Ref. [16]
Water	R B_1	6.471	6.409
	R A_2	7.693	7.669
	R A_1	8.624	8.550
	R B_1	8.897	8.869
Formaldehyde	V A_2	3.718	3.549
	R B_2	5.954	5.838
	V A_1	6.751	6.639

Fig. 4. Time [s] for a single SCF iteration on 32 CPUs of a IBM p690

performed for the optimization procedures. We currently do not make use of sparsity in this part of the program and therefore an asymptotic cubic scaling is expected.

The last performance test is a single point energy calculation of the unit cell of the crambin molecule. This small peptide has 46 residues and crystallizes in a unit cell with two molecules. The calculation included 1284 atoms. With the use of pseudopotentials we arrive at 3626 electrons in the system. The basis sets are of double-zeta polarization (*DZVP*) and triple-zeta double polarization (*TZV2P*) quality, resulting in a total of 11'652 and 20'058 basis functions, respectively. The calculations needed 142 sec and 324 sec per SCF cycle on a single frame (32 CPUs) of an IBM p690, demonstrating again that full DFT simulations of systems with more than 1000 atoms are feasible using the GAPW method.

Summary

A new implementation of the Gaussian and augmented-plane wave method has been presented. The GAPW method allows for efficient and accurate density functional calculations of small and large molecules either as isolated systems or with periodic boundary conditions. Especially noteworthy is that such calculations can be performed using large basis sets, reaching almost the basis set limit. We showed the accuracy of the approach by comparing total energies and structures with results from standard quantum chemistry codes. Efficiency and scaling was demonstrated on a series of water systems reaching up to more than 3000 atoms and 40'000 basis functions as well as on the unit cell of a small peptide with more than 1000 atoms. It could be shown that calculations of this size can be performed on medium-sized computers, a single frame of an IBM p690 in our case.

The GAPW method provides an ideal starting point for the calculation of molecular properties in the condensed phase, especially molecules in solution. Through its capability to provide all-electron wave-functions also properties that depend on the electron density close to the nuclei are accessible. As a first application we showed the calculation of excitation energies with the linear response approach to TDDFT.

The GAPW method makes it possible to study systems that have been inaccessible to density functional methods so far. It does so without compromising accuracy, even for large systems high quality basis sets can be employed. The GAPW method sets therefore a new standard for electronic structure calculations of large systems.

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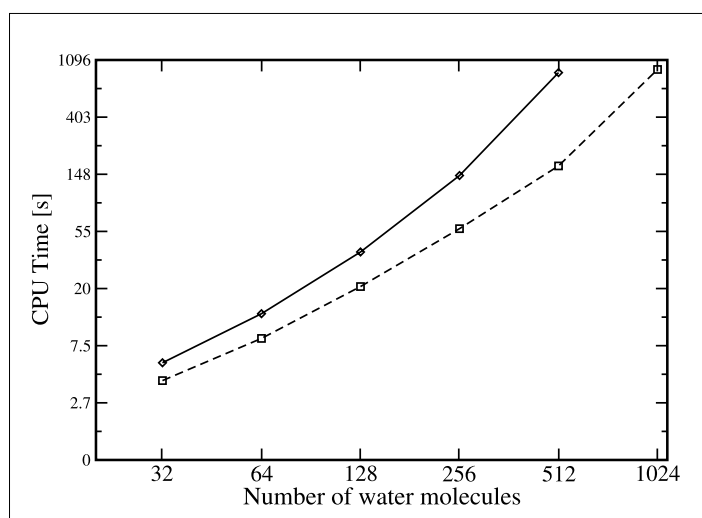[10] M. Krack, M. Parrinello, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2105.
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