



Evaluating Hellmann–Feynman forces within non-local pseudopotentials[☆]

Matyáš Novák^{a,b,c}, Jiří Vackář^a, Robert Cimrman^{b,*}

^a Institute of Physics, Czech Academy of Sciences, v.v.i, Czech Republic

^b New Technologies Research Centre, University of West Bohemia, Czech Republic

^c Faculty of Applied Sciences, University of West Bohemia, Czech Republic

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ABSTRACT

A new approach for evaluating Hellmann–Feynman forces within a non-local potential is introduced. Particularly, the case of Hellmann–Feynman theorem applied within density functional theory in combination with nonlocal ab-initio pseudopotentials, discretized by the finite-element method, is discussed in detail. The validity of the new approach is verified using test calculations on simple molecules and the convergence properties (w.r.t. the DFT loop) are analyzed. A comparison to other previously published approaches to Hellmann–Feynman forces calculations is shown to document that the new approach mitigates, for l -dependent as well as for separable forms of nonlocal pseudopotentials, the efficiency and/or accuracy problems arising in the methods published so far.

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1. Introduction

An efficient evaluation of Hellmann–Feynman forces is essential for geometry optimization tasks and for molecular dynamics calculations in computational material physics. In this paper we introduce the expression for Hellmann–Feynman forces (HF forces, HFF) used in our newly developed ab-initio real-space code for non-periodic electronic structure calculations, based on the density functional theory, finite element method (FEM) (or its variant – isogeometric analysis [1,2]) and non-local environment-reflecting pseudopotentials [3].

The most difficult part of the Hellmann–Feynman forces calculation is the evaluation of the term coming from the gradient of nonlocal pseudopotentials, because the derivative of the pseudopotentials includes not only the derivative of the potential itself, but also the derivative of the projection operators to l -subspaces. We propose a new expression for computing this part of the force, based on differentiating the wavefunctions instead of the projectors.

The new expression is verified by comparing equilibrium atomic positions (i.e. positions with zero forces) to minima of total energies and to experimental values, for nitric oxide, carbon dioxide and tetrafluoromethane and by comparing vibrational

frequencies of carbon dioxide. The convergence property of the expression is analyzed and the expression is compared to other previously published approaches to the non-local contribution to HF forces as regards accuracy and computational demands. This comparison shows advantages in accuracy or/and computational efficiency compared to so far published formulas.

Section 2 provides a short derivation of the basic formula for calculating the Hellmann–Feynman forces. In Section 3 we describe our efficient and numerically stable way for evaluating the local part of the Hellmann–Feynman forces within the finite element method. Section 4 gives a brief overview of various approaches to calculations of nonlocal components of HF forces and illustrates the importance of incorporating all subcomponents of the nonlocal parts. Because none of the methods for evaluating the nonlocal HF forces components published so far has proved to be fully satisfactory in our case, we derived a new formula, which is described in Section 5. Section 6 presents results of sample calculations that demonstrate the correctness of the formula. The error of the computed HF forces is analyzed with respect to the stopping criteria of the DFT self-consistent loop. Section 7 contains a brief convergence and error analysis of the new formula in comparison with other approaches.

2. Hellmann–Feynman forces for nonlocal pseudopotentials

Hellmann–Feynman forces are the gradients of total energy (including the interaction energy of atomic cores) with respect to the movement of atomic centers.

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* Corresponding author.

E-mail addresses: novakmat@fzu.cz (M. Novák), vackar@fzu.cz (J. Vackář), cimrman3@ntc.zcu.cz (R. Cimrman).

The expression for HF forces following from the Hellmann–Feynman theorem (see [4]) seems to be straightforward in principle, since we use the finite element method and therefore a fixed (independent of atomic positions) basis (the standard H^1 elements with the Lagrange polynomial basis [5]). In addition, isogeometric analysis with Bézier extraction [6], ensuring continuity for all quantities up to the second derivative, is available within our code¹ (and can be used if e.g. a floating basis is more efficient in geometry optimization/molecular dynamics calculations). Thus, there is no need for evaluating the so called Pulay forces or the incomplete basis set terms [8].

However, the nonlocality of l -dependent pseudopotentials brings similar problems as the moving basis dependent on atomic positions: The motion of atomic centers leads to the necessity of differentiating projections to l -subspaces, in which case the numerical errors arise due to the singularities of the gradients of spherical harmonics.

According to the Hellmann–Feynman theorem [9], supposing that the fixed discretization basis is used, the forces can be calculated from the gradient of the Hamiltonian

$$\vec{f}_i = -\nabla e_{\text{TOT}} = -\nabla \sum_i w_i \int \psi_i^\dagger H \psi_i = \sum_i w_i \int -\psi_i^\dagger (\nabla H) \psi_i \quad (1)$$

or in bra-ket notation

$$-\nabla \sum_i w_i \langle \psi_i | H | \psi_i \rangle = -\sum_i w_i \langle \psi_i | \nabla H | \psi_i \rangle, \quad (2)$$

where the gradient is considered with respect to the shift of atomic centers. It should be noted that although the proof of the Hellmann–Feynman theorem seems to be a straightforward and uncomplicated application of the variational principle [10], such a simple approach is based on a bit vague assumptions. The exact proof requires a bit more mathematical work [11].

If the basis depends on the positions of atomic centers, the so called Pulay forces or incomplete basis set terms (abbreviated as IBS) arise [8]. In our case (the finite element method), the basis is fixed and we can omit those terms. However, below in this paper we will see a term arising from the gradient of l -projectors, which is similar to the Pulay term, as given here:

$$\begin{aligned} \vec{f}_i &= -\nabla e_{\text{TOT}} = -\nabla \sum_i w_i \langle \psi_i | H | \psi_i \rangle \\ &= -\sum_i w_i \left(\langle \psi_i | \nabla H | \psi_i \rangle - 2 \langle \nabla \psi_i | H | \psi_i \rangle \right). \end{aligned} \quad (3)$$

The total energy in the density functional theory is given by (see e.g. [4,12])

$$\begin{aligned} e_{\text{TOT}} &= \sum_{i=1}^n w_i \int \psi_i^\dagger \frac{1}{2} \nabla^2 \psi_i + \int \psi_i^\dagger V_{\text{EXT}} \psi_i + \int E_H(\rho) \\ &\quad + \int E_{\text{XC}}(\rho) + e_{\text{ION}}. \end{aligned} \quad (4)$$

where w_i are occupation numbers of ψ_i states and V_{EXT} is the external potential – in our case the sum of pseudopotentials of atomic cores, each of them constituted by a long-range local part and a short-range nonlocal l -dependent part:

$$V_{\text{EXT}} = \sum_a \left(V_{\text{LOC}}^a + \sum_l V_{\text{NL}}^{a,l} P_l^a \right), \quad (5)$$

where P_l^a is a projection operator into l -subspace of the a th center.

According to (1) there is no implicit (through the dependence of the wavefunctions) dependence of the HF force on the position of the atomic centers. Therefore the gradient of the total energy contains only terms with the explicit dependence on atom positions:

$$\nabla_a e_{\text{TOT}} = \int \nabla V_{\text{LOC}}^a \rho + \sum_{l,i} w_i \int \psi_i^\dagger \nabla (V_{\text{NL}}^{a,l} P_l^a) \psi_i + \nabla e_{\text{ION}}. \quad (6)$$

3. Local parts of Hellmann–Feynman force

The first term of (6) is the local² part of electron–ion interaction. The gradient of the local ion potential can be easily evaluated as the partial derivative of the potential in the radial space multiplied by the direction from the atomic center:

$$\int \nabla V_{\text{LOC}}^a \rho = \int \frac{\partial V_{\text{LOC}}^a(r)}{\partial r} \frac{\vec{x} - \vec{c}_a}{r} \rho. \quad (7)$$

Only slightly more effort is required to evaluate the last term of (6) expressing the repulsion of atomic cores. Without using pseudopotentials, this term would shrink to the classical Coulombic force between point charges. However, a pseudopotential smooths the charge of the nucleus and the actual force differs from the pure point-charges Coulombic term, as can be seen in Fig. 1. Therefore, the ion–ion force is derived by differentiating the ion–ion term of the total energy expression proposed e.g. in [12].

Expressing the pseudocharge ρ_{ION}^a of the ion a as

$$-4\pi \rho_{\text{ION}}^a = \nabla^2 V_{\text{ION}}^a, \quad (8)$$

we can express the ion–ion energy as

$$\begin{aligned} e_{\text{ION}} &= \frac{1}{2} \sum_{i \neq j} \int V_{\text{LOC}}^i \rho_{\text{ION}}^j = \frac{1}{2} \sum_i \int V_{\text{LOC}}^i \sum_j \rho_{\text{ION}}^j \\ &\quad - \frac{1}{2} \sum_i \int V_{\text{LOC}}^i \rho_{\text{ION}}^i. \end{aligned} \quad (9)$$

Differentiation of e_{ION} yields

$$\nabla_a e_{\text{ION}} = \frac{1}{2} \int \nabla_a V_{\text{LOC}}^a \sum_{j \neq a} \rho_{\text{ION}}^j + \frac{1}{2} \int \sum_{i \neq a} V_{\text{LOC}}^i \nabla \rho_{\text{ION}}^a. \quad (10)$$

The two terms in (10) express the forces corresponding to charge–potential and potential–charge interactions, respectively. The charge–potential and potential–charge forces must be equal, therefore (10) can be evaluated using only one of these terms. The second term of (10) suffers from much larger numerical errors than the first one, because the gradient of ρ_{ION} is in fact the third derivative of V_{LOC} – see (8) – and each differentiation introduces numerical errors into the computation, as can be seen in Fig. 1. That is the reason for using only the first term of (10) to evaluate the ion–ion force:

$$\begin{aligned} \nabla_a e_{\text{ION}} &= \frac{1}{2} \int \nabla_a V_{\text{LOC}}^a \sum_{j \neq a} \rho_{\text{ION}}^j + \frac{1}{2} \int \sum_{j \neq a} V_{\text{LOC}}^j \nabla \rho_{\text{ION}}^a \\ &= \int \nabla_a V_{\text{LOC}}^a \sum_{j \neq a} \rho_{\text{ION}}^j. \end{aligned} \quad (11)$$

4. Nonlocal part of Hellmann–Feynman force

The most difficult term of Eq. (6) is the middle one; the nonlocal part of electron–ion interaction. Denoting $V_l = V_{\text{NL}}^{a,l}$, and

¹ Our code FENNEC (Finite Element Non-periodic Ab-Initio Electronic structure Code) is based on the open source finite element package SfePy [7].

² In the sense that pseudopotential can be split into its local and nonlocal part.

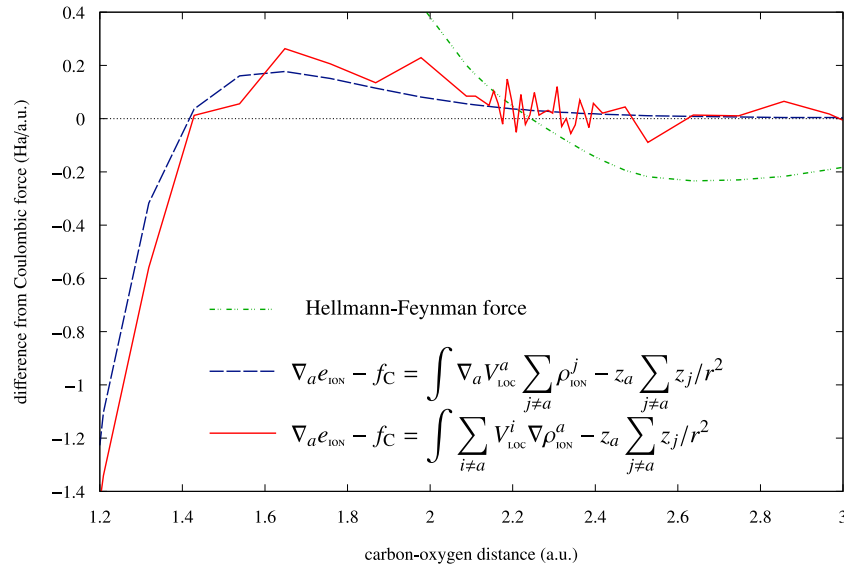


Fig. 1. Two ways of computing ion–ion repulsive forces on carbon pseudocore of CO₂ molecule: Interatomic distances between the carbon atom and oxygen atoms (molecule is stretched symmetrically) are shown on the x axis and differences between the computed force and the point-charges Coulombic force on the y axis. Note the numerical instabilities for the second method and the fact, that the pseudocore ion–ion forces differ substantially from the Coulombic force in common interatomic distances. (Stronger oscillations of the second method around the expected equilibrium are caused by a finer sampling in this region).

taking a sample ψ , the corresponding force coming from a given l can be expressed as

$$\langle \psi | \nabla_a (V_l P_l) | \psi \rangle = \langle \psi | (\nabla_a V_l) P_l | \psi \rangle + \langle \psi | V_l (\nabla_a P_l) | \psi \rangle, \quad (12)$$

where P_l is a projection into the given l -subspace using integrations over spheres

$$P_l | \psi \rangle = \sum_m Y_{l,m} \int_{\theta, \varphi} Y_{l,m} \psi = \sum_m |Y_{l,m}\rangle \langle Y_{l,m} | \psi \rangle. \quad (13)$$

The first term in (12) expresses a force originating from the shift of the potential and the second term expresses the change of the charge density in the given l -subspace that occurs due to the shift of the centers of the l -projections.

While the first term of (12) can be evaluated by means of spherical projections relatively easily, the second one is more difficult. If we differentiate the projector P_l , we obtain the gradient of the spherical harmonic functions

$$\nabla_a P_l = \nabla_a \sum_m |Y_{l,m}\rangle \langle Y_{l,m} | = \sum_m (|\nabla_a Y_{l,m}\rangle \langle Y_{l,m} | + |Y_{l,m}\rangle \langle \nabla_a Y_{l,m} |), \quad (14)$$

with a singularity (for $l > 0$) at the origin. The approaches used so far have applied various strategies to overcome this difficulty. In the original article describing the computation of Hellmann–Feynman forces [4] within DFT, the gradient of $Y_{l,m}$ is silently neglected. In some later works, as e.g. in Quantum Monte Carlo methods [13], where similar projections occur, authors explicitly claim that such terms can be neglected. However, in our case, this term forms a substantial part of the force and must be included into the HFF computation, as can be seen in Fig. 2.

Various ways have been used to avoid the necessity to calculate this problematic term within the approaches to HFF described in literature: the analytic derivatives of plane waves are used in [16,17]; the Kohn–Sham equations are used in [18] to avoid the necessity to differentiate the nonlocal parts of the force, which however implies the necessity to differentiate the sum of Kohn–Sham energies. It would be neither simple nor computationally efficient in our case. Another alternative, evaluating the special integrals over atomic spheres like in the LAPW

method [19], would be too computationally expensive within the general finite element basis.

Probably the closest approach to our one has been published in [20,21] for evaluating Hellmann–Feynman forces for the case of a separable (or Kleinman–Bylander [22]) form of the pseudopotential $v_{l,n}$. That approach yields the following term for the nonlocal energy

$$\nabla e_{\text{NL}} = 2 \text{Re} \sum_i w_i \sum_{n,l,m} \langle \psi_i | v_{l,n} Y_{l,m} \rangle \langle \nabla (v_{l,n} Y_{l,m}) | \psi_i \rangle. \quad (15)$$

In some cases, the gradient of the projectors can be expressed analytically (e.g. see [23] or [24]), but for a general separable pseudopotential, the radial part must be differentiated numerically.

As the authors of [25] recommend, an improved precision can be achieved if the projector is decomposed using the vector spherical harmonic functions $Y_{l,m} r$ (where r is the radius):

$$\nabla v_{l,n} Y_{l,m} = \nabla \left(\frac{v_{l,n}}{r} Y_{l,m} r \right) = \left(\nabla \frac{v_{l,n}}{r} \right) Y_{l,m} r + \frac{v_{l,n}}{r} \nabla (Y_{l,m} r), \quad (16)$$

because such decomposition makes the angular projector analytical in the origin. As we will see later in Fig. 8C, this approach is less suitable for the case of l -dependent form of the pseudopotentials (15), because the radial part must be divided by r^2 and consequently the numerical accuracy decreases.

It seems, that RMG code [26] maybe use a method similar to our approach to avoid differentiating of projectors. However, the papers describing the method, e.g. [27], cited by the RMG web page, contain just differentiating of projectors without further details of this issue.

5. Evaluating HFF using derivatives of wavefunctions

Since none of the methods mentioned above is fully satisfactory in our case, we propose another way to calculate the nonlocal terms of HF forces. Our approach is based on the simple assumption that the movement of an atomic core in any direction must result in the same force as the movement of the wavefunction

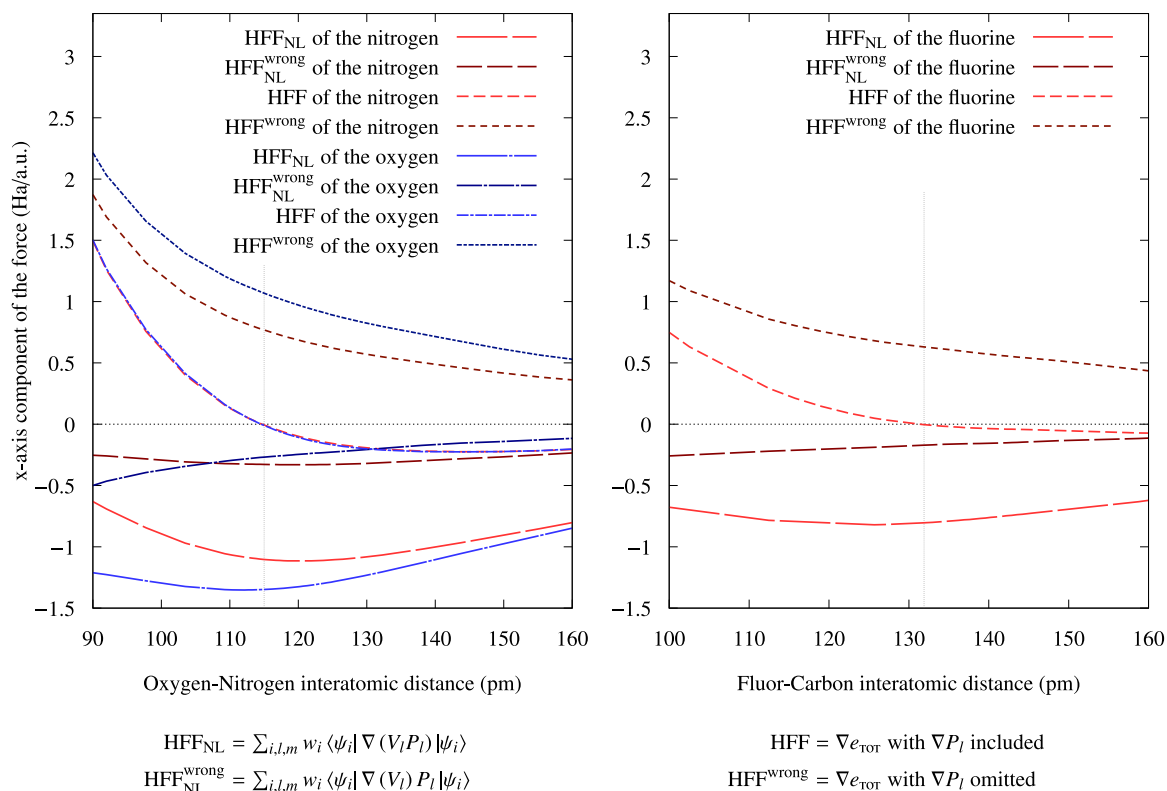


Fig. 2. The importance of the l -subspace projectors' derivatives in Hellmann–Feynman forces: Computed HF-forces and their nonlocal components acting on the oxygen and nitrogen atoms in a nitric oxide molecule and on the fluorine atom in tetrafluoromethane, with and without the l -subspace projectors' derivatives. The expected interatomic distance (vertical dashed line) is 115 pm for nitric oxide [14] and 131.91 pm for CF_4 [15].

(which is “frozen” due to the Hellmann–Feynman theorem) in the opposite direction. So instead of differentiating the operator V_l (as in (14)), making use of the Hermiticity of the V_l operator we can state

$$\begin{aligned} \langle \psi | \nabla_a V_l | \psi \rangle &= -\nabla_\psi \langle \psi | V_l | \psi \rangle = -\langle \nabla \psi | V_l | \psi \rangle - \langle \psi | V_l | \nabla \psi \rangle \\ &= -2 \text{Re} \langle \nabla \psi | V_l | \psi \rangle, \end{aligned} \quad (17)$$

or, in the case of the separable form of a pseudopotential,

$$\nabla e_{\text{NL}} = -2 \text{Re} \sum_i w_i \sum_{n,l,m} \langle \psi | v_{l,n} Y_{l,m} \rangle \langle v_{l,n} Y_{l,m} | \nabla \psi_i \rangle. \quad (18)$$

Since the derivative terms of (17) and (18) are already expressed in the finite element basis, there are no extra computational demands for evaluating the projection into the basis and no additional inaccuracies arise because the analytic derivatives of the element basis functions are available. Moreover, the same expression can be easily used both for the l -dependent and separable pseudopotentials.

Note that the expression (17) a bit resembles the incomplete basis set correction (or the Pulay term, see Eq. (3)). Although the formal expressions seem to be (almost) the same, they express different things. Whereas in our case the differentiation represents a spatial shift of wavefunctions (in the stable basis), the Pulay term means “how the wavefunction changes due to the change of the basis”. Thus the operator ∇ represents different differential operator in the two equations: since our basis does not depend on atomic positions, the Pulay term is zero in our case, but the expression (17) is not.

To summarize, the Hellmann–Feynman force within the finite element method (FEM) in real space can be simply expressed and

evaluated as

$$\begin{aligned} \nabla e_{\text{TOT}} &= \int \rho \nabla V_{\text{Loc}} - 2 \sum_i w_i \text{Re} \int \nabla \psi_i^+ \sum_{j,l} V_{\text{NL}}^{j,l} \psi_j \\ &\quad + \int \sum_{a \neq k} \nabla V_{\text{Loc}}^k \rho_{\text{ION}}^a. \end{aligned} \quad (19)$$

6. Verification of the HFF formula and its convergence

We have verified and tested our newly developed expression for the molecules of nitric oxide, carbon dioxide and tetrafluoromethane, with interatomic distances scaled by a variable factor β .

Hexahedral meshes, with cubical elements near atomic sites with the edge length α , and substantially larger elements in distances greater than 2.4 a.u. from atomic centers were used for the calculations below. The distance from any atomic center to the domain boundary was at least 16 a.u.

The convergence of the calculated HF forces and their dependence on the inter-atomic distance for the carbon dioxide molecule is plotted in Fig. 3. The relative shift of the equilibrium interatomic distance with respect to the experimental value (116.3 pm, see [14]) is 0.82, which is comparable to the other methods and is in the expectable range if we consider applying DFT with a simple form of the XC-functional for a molecule.

The next a bit surprising result was that the computed HF forces were much smoother, evincing much smaller fluctuations, than the numerical derivative of calculated total energy. As the magnitude of fluctuations of total energy is greater than the difference between the numerical derivative of total energy and calculated HF forces, we can conclude that the calculated HF forces

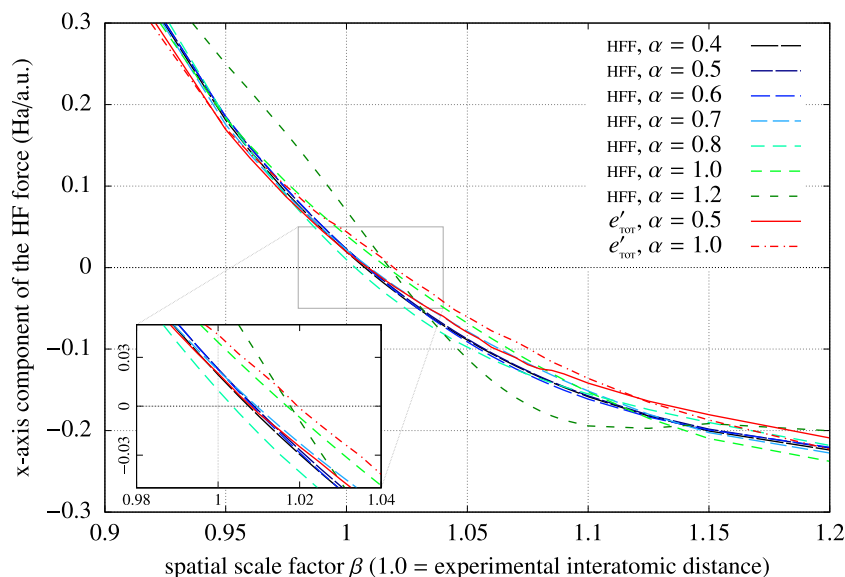


Fig. 3. The calculated HF force acting along the x -axis on the first oxygen atom in carbon dioxide, varying with the mesh size (the parameter α is the linear size of the smallest element, in atomic units). e'_{TOT} denotes the derivative of the total energy w.r.t. the interatomic distance, divided by two (stretching of the molecule affects two oxygen-carbon interactions). The red e'_{TOT} curves correspond to HFF calculated by differentiating the total energy numerically; there the wavefunctions are recalculated for each change of atomic position. We provide those curves for comparison with the HF-theorem-based curves, where the wavefunctions are frozen.

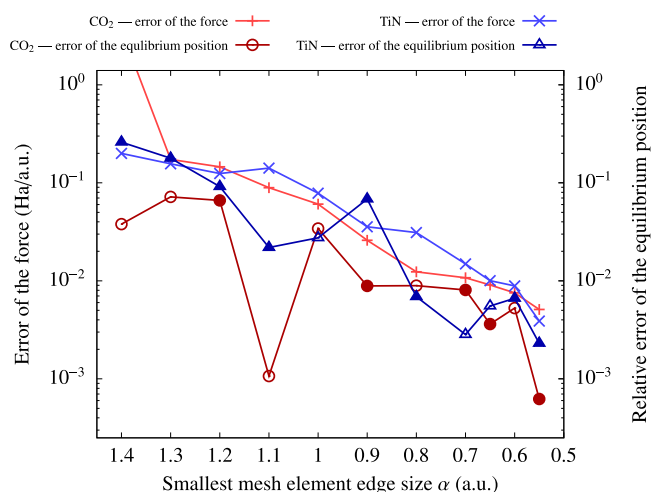


Fig. 4. The convergence of HF interatomic force in CO_2 molecule and in diatomic TiN, with regard to the mesh element size. The reference value is the force for the finest mesh ($\alpha = 0.45$). β denotes spatial scale factor for interatomic distances w.r.t. the equilibrium position. Error is computed as the L^2 norm of the function $f_\alpha(\beta) - f_{\text{ref}}(\beta)$ on interval $(0.7, 1.4)$. Positive/negative errors of equilibrium positions are represented by full/empty circles or triangles. The reference value for the equilibrium distance of TiN is taken from the most precise calculation since the diatomic TiN cannot be compared with common data for crystalline TiN in this respect.

agree with the numerical derivatives of total energy within the precision of our total energy calculations and that our approach offers a numerically stable way to calculate HF forces.

The convergence of the HF forces and the equilibrium position among atoms in CO_2 molecule with regard to the mesh element size is shown in Fig. 4. The reference values were those obtained for the finest mesh ($\alpha = 0.45$).

The results of similar accuracy have been achieved for HF force in nitric oxide molecule and tetrafluoromethane molecule, where the relative errors of expected interatomic distances were only 0.232% and 0.15% w.r.t. the expected values of 115 pm [14] and

131.91pm [15], respectively, and the inaccuracy of the obtained distance of zero HF forces with respect to the computed minima of total energy was less than one per mille. The calculated HF forces for both molecules can be seen in Fig. 2.

We would like to emphasize that the experimental values above were used just as reference values for comparing the calculations mutually, without making a greater effort to obtain the best agreement with experimental values. Such an effort – including the use of more sophisticated exchange–correlation term and pseudopotentials tuning – would lead to even more precise and numerically more stable results.

We also verified the convergence of HF forces w.r.t. the interatomic distance in the diatomic titanium nitride, in order to test the convergence also for transition metals. Figs. 4, 5 show that the errors in the case of diatomic titanium nitride converge in a similar manner as in the case of carbon dioxide. The convergence with the mesh element size for TiN seems to be slower than for CO_2 , but it should be noted that it always depends on the parameters of the used pseudopotential – softer and less transferable pseudopotentials generally converge faster.

For a stricter verification of our code for HF forces and of its convergence properties we have calculated vibrational frequencies of the symmetric mode (often called ν_1 , see [28]) of carbon dioxide molecule. As the vibrational frequency is in fact a derivative of HF force (and second derivative of total energy), it is usually much more sensitive to the computational errors than equilibrium position and therefore it is a suitable benchmark for the precision of the method.

The vibrational frequencies have been calculated from the force acting on carbon atom displaced by 0.005 a.u., using a simple model of linear harmonic oscillator. Our results match the data obtained from the experiment [29] quite well and document good convergence properties of our proposed formula – see Fig. 6.

We also tested the dependence of the error in HF forces (w.r.t. reference values obtained from self-consistent states) on the degree of convergence of the DFT loop (i.e. on the precision of the solution of Kohn–Sham equations). Our calculations show nearly linear dependence of the size of the HFF error on the L^2

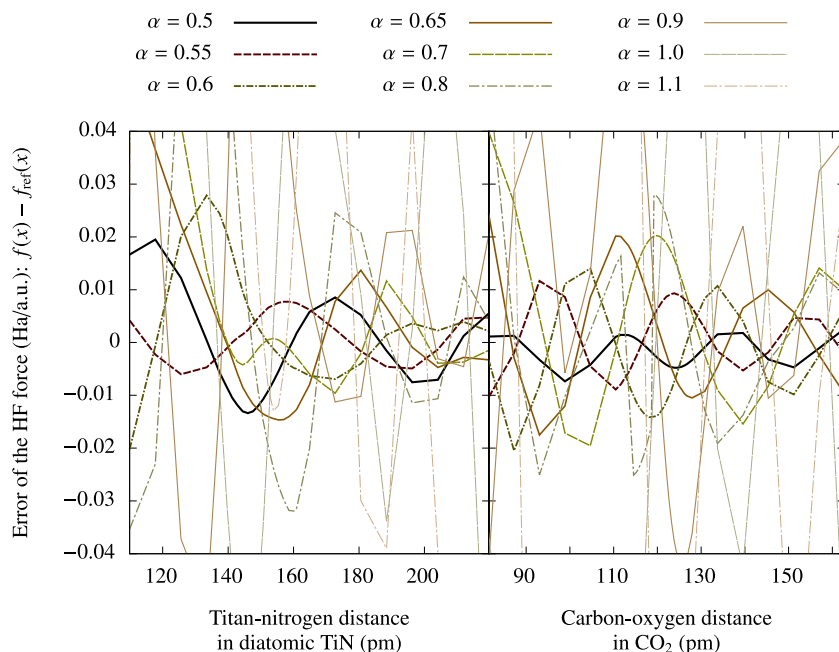


Fig. 5. Comparison of convergence of the HF-forces for diatomic titanium nitride and carbon dioxide. The parameter α is the edge length of the smallest elements of the mesh. The reference force f_{ref} is the force for the finest mesh ($\alpha = 0.45$).

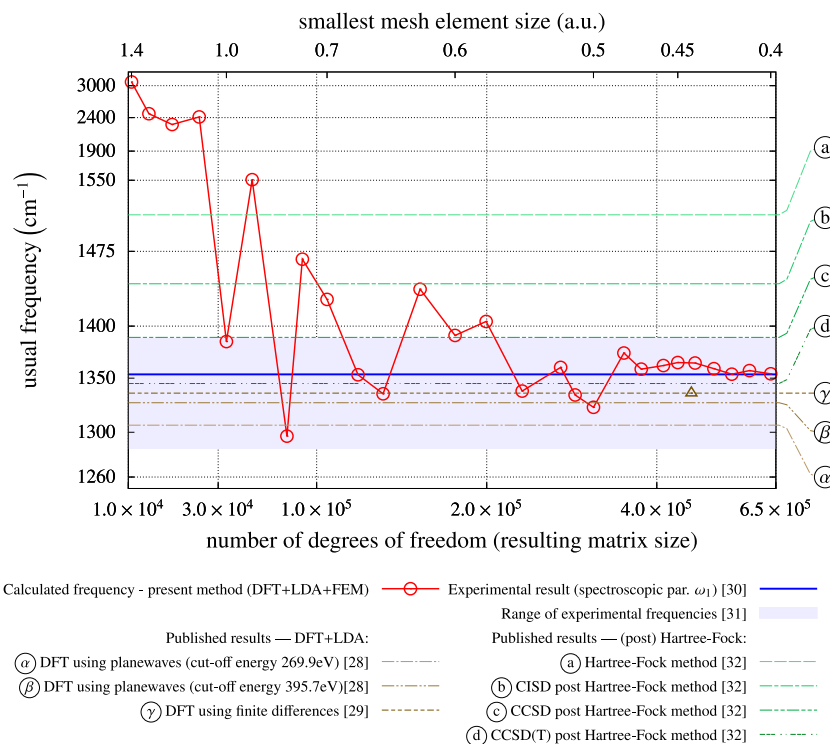


Fig. 6. Convergence of symmetric vibrational frequencies of CO_2 molecule with respect to the mesh element size and number of degrees of freedom, compared to other published experimental and computed results. Axis is in logarithmic scale, with compressed region below 10^5 (on the x-axis) and above 1550 (on the y-axis) to cover whole convergence curve while emphasizing the region relevant to the most accurate results. The convergence properties of the calculations done by other methods, even if the numbers of degrees of freedom are indicated in the references, can be roughly compared only in the case of finite differences (denoted by Δ), because of essentially different character of bases and of resulting matrices in the other methods.

norm of the DFT error, see Fig. 7, regardless of the system and/or spatial stretching of the system. This dependence can be used as a reasonable estimate of the error of the computed HF forces. It can be also used for determination of the stopping criteria for the DFT loop, e.g. in geometry optimizations of more complex systems.

7. Convergence and fluctuations of various methods for computing HF forces

A series of calculations to compare the errors and convergence rates of six methods for evaluating the nonlocal components of

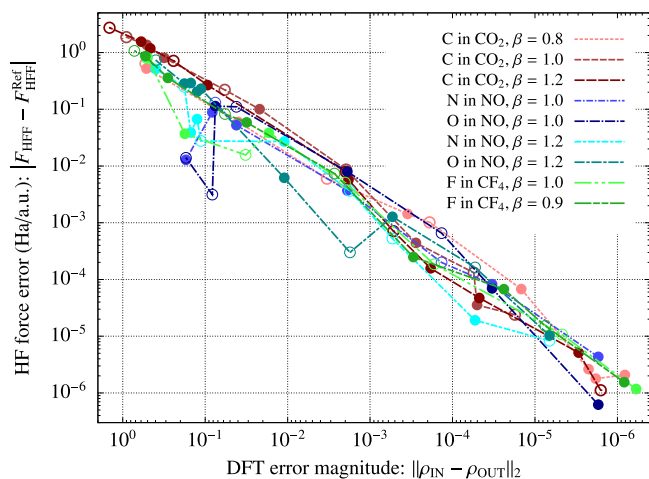


Fig. 7. Convergence of HF forces with respect to the stopping criterion of the DFT loop. The DFT error magnitude is computed as L^2 norm of the difference between the input and output charge densities of each DFT iteration. The HF forces from the last – fully converged (DFT error magnitude $< 10^{-7}$) – step of the DFT loop serve as the reference forces $F_{\text{HF}}^{\text{Ref}}$. Empty/full points denote negative/positive differences to the reference values. β is the spatial scale factor (stretching the molecule). The Anderson/Pulay mixing scheme [30,31] was used in the DFT loop to achieve the self-consistent state.

Hellmann–Feynman forces is shown in Fig. 8. Using the series of meshes with varying base element length α (described in the previous section), we compare the results of various methods and assess these results in comparison with reference values obtained for the finest mesh ($\alpha = 0.7$). We can see that all the methods converge to the same solution. This solution is smooth and corresponds to the derivative of the total energy (as verified in the previous section).

Four of the compared methods use separable pseudopotentials (A, B, C, E in Fig. 8) and two of them use l -dependent pseudopotentials (D, F). The methods A to D express HF-forces directly using the HF theorem (1), where the methods A and D use the approach proposed in this paper, i.e. differentiating of the wavefunctions (for separable and l -dependent pseudopotential, respectively), whereas B and C differentiate the projectors of the separable pseudopotentials – here the singularity of the analytical gradient of the separable pseudopotential is treated by projecting into the FEM basis (B) or using the vector spherical harmonics for $l > 0$ (C, see (16)).

On the other hand, methods E and F use the numerical differentiation of the total energy in separable (E) and l -dependent (F) pseudopotentials. In both cases, wavefunctions – according to the HF theorem (1) – remain “frozen” during differentiating.

We do not consider the numerical differentiation of the total energy with non-frozen wavefunctions (i.e. without employing the HF theorem) in this section. The need of recalculating wavefunctions for various atomic positions made such methods uncompetitive as regards both efficiency and accuracy: computational demands and the inaccuracies of wavefunctions (numerical as well as arising from non-fully converged DFT-loop or incompleteness of the FEM basis, see Fig. 3) practically disqualify this approach.

Fig. 8 is complemented by Table 1 showing the asymptotic complexity of operations of the considered methods in terms of the discretization parameters.

7.1. Discussion of the methods

In the following section we will assess the accuracy of the considered methods, taking the computational demands into account. Note that the oscillations – that can create false local

Table 1

The asymptotic complexity of the methods considered in Fig. 8 for computing the non-local part of the HF-forces acting on one atom, in terms of the discretization parameters. Both Θ_E and Θ_P cannot be easily expressed using quantities above, as they depend in a complicated way on the mesh geometry (especially the dependence of Θ_E on n_e is strongly non-monotonic for various meshes covering the same spatial volume, as can be seen in Fig. 8 D and F). The short range of nonlocal pseudopotential components is not employed in the expressions above; by employing that feature, n_e would correspond only to the number of elements within the nonlocal pseudopotential component support.

Symbol	Meaning
n_ψ	Number of ψ_i
n_p	Number of projectors of separable pseudopotential of the atom
n_{lm}	Number of l, m components of l -dependent pseudopotential
n_e	Number of elements of the FEM mesh (function of the α in the graphs above)
n_{qp}	Number of quadrature points in each element
n_{bf}	Number of basis functions in a single finite element
n_{fd}	Number of points used for numerically differentiating e_{tot}
n_{rp}	Number of points in the radial mesh for the projection of the wavefunctions into the L -space
n_{ap}	Number of points in the angular mesh for the projection of the wavefunctions into the L -space
Θ_P	L^2 asymptotic complexity of the projection into the FEM basis
Θ_E	Asymptotic complexity of evaluating a quantity in the FEM basis in a given point
Method	Asymptotic computational time complexity
A	$n_\psi n_p n_e n_{bf} + n_p n_e n_{qp} n_{bf}$
B	$n_\psi n_p n_e n_{bf} + n_p n_e n_{qp} n_{bf} + n_p \Theta_P$
C	$n_\psi n_p n_e n_{bf} + n_p n_e n_{qp} n_{bf}$
D	$n_\psi n_{lm} n_e n_{qp} + n_\psi n_{lm} n_{rp} n_{ap} \Theta_E$
E	$n_{fd} n_\psi n_p n_e n_{bf}$
F	$n_{fd} n_\psi n_{lm} n_e n_{qp} + n_{fd} n_\psi n_{lm} n_{rp} n_{ap} \Theta_E$

minima or spoil the convergence of the minimization algorithm – might interfere the accuracy of the whole computation more than a constant error that only shifts the equilibrium position a bit. From this point of view, a worse precision has been achieved using the expressions that differentiate the separable pseudopotential, either analytically or numerically (see Fig. 8C and E), compared to those using the gradient of wavefunctions (A and D).

From the anti-hermiticity of the bilinear form $(* \cdot \nabla *)$ follows

$$\text{Re}(\nu_{l,n} Y_{l,m} \cdot \nabla \psi_i) = -\text{Re}(\nabla \nu_{l,n} Y_{l,m} \cdot \psi_i) \quad (20)$$

and therefore that the computation using the gradient of projector (Fig. 8C) is mathematically equivalent to our presented method (differentiating ψ , Fig. 8A). The two cases differ only by numerical errors caused by the differentiation: while using derivatives of a separable pseudopotential leads to integrating previously differentiated projectors of the separable pseudopotential, our new method allows to do both steps – differentiating and integrating – “at once” during the FEM assembling. Moreover, the basis functions have polynomial derivatives that are more suitable for the numerical quadrature [32] used in the FEM assembling than the derivatives of projector functions of the separable pseudopotential. Thus, it is no surprise that our proposed method results in smaller numerical fluctuations as can be seen by comparing Fig. 8A and C.

The poor numerical precision of differentiating separable pseudopotentials (Fig. 8C and E) can be improved by projecting the pseudopotentials into the FEM basis prior to the differentiation, as in (Fig. 8B). This approach eliminates both sources of errors noted in the previous paragraph. Since the pseudopotentials can be projected into the FEM basis quite precisely, the resulting error is nearly the same as in our proposed method (Fig. 8A). However, the projections of pseudopotentials into FEM basis are computationally expensive, whereas the projections of wavefunctions have been already prepared. Therefore, our

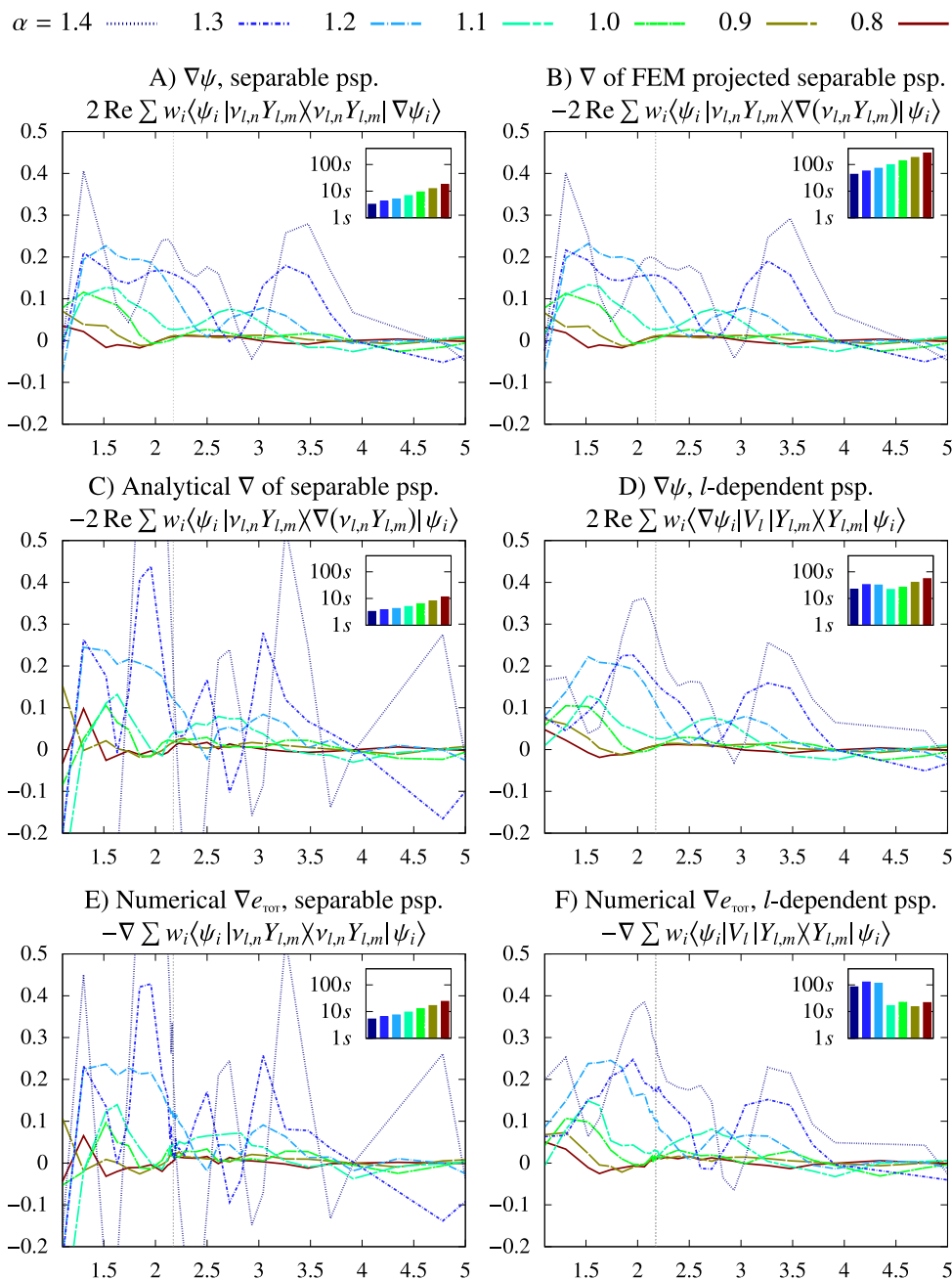


Fig. 8. Convergence of the HF-force acting on N atom in NO molecule with the mesh element size (the parameter α is the linear size of the smallest element, in atomic units) for various approaches. The curves show the numerical error of HFF (in Ha/a.u.) related to the reference force obtained using the finest mesh. The x axes show the interatomic distance (in a.u.), with equilibrium marked by the vertical dotted line. Small subgraphs show the computational time in a logarithmic scale.

newly proposed method provides a significant improvement in computational efficiency compared to that approach.

The results obtained using l -dependent potentials (Fig. 8D and F) do not suffer from the inaccuracy of the gradient evaluation, but they have another disadvantage: evaluation of the spherical integrals (we use Lebedev quadrature for integration on spheres, see [33]) is not a natural approach for the finite element method, therefore its computational expenses do not depend on the mesh size. Or even worse: for smaller meshes with larger elements, the projection from real space to the reference element, that is necessary for evaluating the integral, can be more demanding than for finer meshes.³ This behavior, that may look strange

³ Our additional numerical tests show a strong dependence of the computational demands on the geometry of the used mesh.

at first sight, is caused by the fact that the same number of integration points for the radial integration is needed for a fine and for a coarse mesh. Solving the L^2 projection on larger elements of the coarse mesh can require more computational time to achieve the same accuracy of interpolation than solving the same problem on a finer mesh. This behavior is very disagreeable because it interferes with using a coarse mesh as a fast and cheap preprocessing for obtaining a reasonable guess for initial positions of atoms.

In some cases, the numerical derivative of the total energy using the l -dependent pseudopotentials (Fig. 8F) offers better computational efficiency than the newly proposed method. However, none of the methods was implemented with all possible optimizations. In addition, when using a particular HFF evaluation method in combination with a particular electronic-structure

code, the efficiency of HFF evaluation depends very much on which quantities have been already precalculated in the code for other purposes. Therefore the presented computational times are only indicative and they can serve more to show how the computational time scales with the system size, than to compare the methods mutually. The computational expenses for evaluating the matrix elements of separable pseudopotentials can be substantially reduced by taking the full advantage of the short-ranged nature of the non-local pseudopotential components, evaluating the integrals only on the mesh elements within the spatial scope of the nonlocal part of each pseudopotential; in that case, n_e in Table 1 would correspond only to the number of elements within the nonlocal pseudopotential component support. It could clearly reduce the computational expenses for evaluating the integrals substantially (as the experience with similar techniques from other codes, e.g. [26,34], confirms), whereas the similar way in the case of l -dependent pseudopotentials – the short range radial mesh – has been already employed in the above calculations.

Moreover, the l -dependent pseudopotentials provide a worse precision near the equilibrium position according to our test calculations. Last but not least, the numerical derivatives of the total energy suffer from much stronger fluctuations (due to the inaccuracies of the numerical differentiation), i.e. they are not as smooth, compared to the forces obtained by differentiating the wavefunctions, as can be seen in Fig. 8 near the equilibrium position (where the forces were calculated for varying interatomic distances with a fine step).

Therefore we conclude that the method A – differentiating the wavefunctions with the separable pseudopotentials – seems to be the most suitable method for applications within the FEM combined with the non-local potentials. The proposed approach offers both the sufficient numerical accuracy and the computational efficiency and outperforms the other methods considered within the scope of this study.

7.2. Notes on efficiency with respect to other codes

The accuracy of the calculations increases with decreasing the parameter α (the smallest mesh edge length), while the problem size in terms of the number of degrees of freedom (DoF's) increases as well, proportional to $1/\alpha^3$. More DoF's usually lead to higher computational demands, but, in the FEM basis, the efficiency is affected not only by the number of DoF's, but also by the number of non-zero elements in Hamiltonian matrix, by the number of the rank- k updates, by the computational demands of projecting quantities to the basis and by computational demands for finding the reference element coordinates of points in general positions (the last factor can be hardly expressed in terms of the DoF's number, because for large elements the solutions are often not faster than for a larger number of smaller elements). Therefore – with respect to more general aims of the paper – we want to avoid dealing with the details too specific for particular basis types. In addition, seen from the viewpoint of the overall computational time, the HFF evaluations are not the bottleneck for most codes, including FENNEC (in our benchmarks, the HFF evaluation takes a few per cent of the total elapsed time: below 1% for the largest of the tasks solved above, and it diminishes progressively with increasing problem size). For the relevance of comparison of particular HFF evaluation algorithms, their precision, numerical stability and the absence of oscillations are much more important factors, which we tried to demonstrate in the paper.

Study limitations. Deliberately we neither give the comparison of the efficiency of our code⁴ for calculating electronic structure as a whole with other codes nor we associate the algorithms for evaluating non-local potential components listed in Fig. 8 with particular other codes. That association could be disputable since many authors do not state how they solve this problem, and even if they have indicated something in past, it could have been changed. Our capabilities and the objective feasibility to analyze other codes (to determine which algorithms they actually use) are limited and our goal is not to criticize other codes, much less to decide which one of other codes can be classified as a comparative standard. In this paper we focus on a particular problem – evaluating HFF in a potential with non-local components – and we try to give an overview of algorithms and approaches to solve that problem that is common for (at least) all the methods employing pseudopotentials, which has not been – to our knowledge – published so far.

8. Conclusion

In this paper we present a new approach for calculating the Hellmann–Feynman forces in non-local pseudopotentials discretized using the finite element method, within the density functional theory. The correctness of the present method and numerical properties of the newly proposed formula have been demonstrated by calculations on simple molecules.

Also, very advantageous convergence properties of the newly proposed formula have been demonstrated, which can be used for a reasonable guess of computational error due to misconvergence of the DFT loop and for determination of the proper value for stopping criteria for the DFT self-consistent loop.

Special attention have been focused on the nonlocal part of the Hellmann–Feynman force formula. For that, the precision and computational efficiency were compared to other methods such as numerically differentiating the total energy and other approaches published up to now for evaluating the Hellmann–Feynman forces. This comparison documents that the proposed approach cures the performance and precision problems that arise in other methods, both for the l -dependent and separable forms of non-local pseudopotentials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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⁴ The FENNEC code is still in the pre-release stage: we plan to describe it properly together with releasing the whole code as an open-source.

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