Nonvanishing quadrature derivatives in the analytical gradients of density functional energies in crystals and helices

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ABSTRACT
It is shown that the quadrature derivatives in some analytical gradients of energies evaluated with a multi-centre radial-angular grid do not vanish even in the limit of an infinitely dense grid, causing severe errors when neglected. The gradients in question are those with respect to a lattice constant of a crystal or to the helical angle of a chain with screw-axis symmetry. This is in contrast with the quadrature derivatives in atomic gradients, which can be made arbitrarily small by grid extension. The disparate behaviour is traced to whether the grid points depend on the coordinate with respect to which the derivative of energy is taken. Whereas the nonvanishing quadrature derivative in the lattice-constant gradient is identified as the surface integral arising from an expanding integration domain, the analytical origin of the nonvanishing quadrature derivative in the helical-angle gradient remains unknown.

1. Introduction
The analytical energy gradient method of density functional theory (DFT) [1, 2] is one of the most heavily used computational machineries in chemistry. It serves as an essential infrastructure of chemical research, upon which its accuracy, efficiency, and stability have a great impact.

The method is based on Pulay’s formalism [3] of the analytical energy gradients for Hartree–Fock (HF) theory. In DFT, an additional term emerges from the exchange-correlation (XC) energy, which is often evaluated by quadrature using Becke’s interlocking multi-atom-centre grid [4] (see also Satoko [5]). Its formulation was first reported by Delley [6], who not only established a method for computing these XC energy gradients but also pointed out the existence of a correction due to the variations in grid coordinates and weights. Delley and coworkers [6, 7] deemed this correction negligible in atomic gradients. Johnson, Gill, and Pople [8] reported
an implementation fully accounting for these quadrature derivatives. Johnson and Frisch [9], Malagoli and Baker [10], and more recently Shang and Yang [11] all concluded that the quadrature derivatives are nonnegligible in vibrational frequencies, although they are generally small and can be made arbitrarily smaller by increasing grid size.

The objective of this article is to point out surprising cases where the quadrature derivatives are large and nonvanishing even in the limit of an infinitely dense grid, causing severe errors when they are neglected. This problem manifests itself in the atomic-basis-set DFT for crystals and helices [12, 13].

2. Quadrature derivatives

Let us take an infinite helical polymer (screw axis along \( x \) with lattice constant or ‘rise’ \( a \) and helical angle or ‘twist’ \( \theta \) [14]) as our example [12, 13]. The atomic positions in the \( n \)th helical repeat unit cell (hereafter simply ‘cell’) are rotated anticlockwise by \( n\theta \). Therefore, the coordinates of the \( I \)th atom in the \( n \)th cell are related to those in the zeroth cell by

\[
X_{I(n)} = X_{I(0)} + na, \\
Y_{I(n)} = Y_{I(0)} \cos n\theta - Z_{I(0)} \sin n\theta, \\
Z_{I(n)} = Y_{I(0)} \sin n\theta + Z_{I(0)} \cos n\theta.
\]

The formulation for this system encompasses molecules (where nonvanishing quadrature derivatives do not occur), linear (nonhelical) polymers, and two- and three-dimensional crystals. Spin-restricted hybrid DFT formalism [12, 13, 15, 16] for the energy per cell is given in Appendix 1. For a more complete formalism of the analytical energy gradient with respect to \( \theta \), see Appendix 2. Here, we focus our attention on the quadrature derivatives in the XC energy gradients. Atomic units are used throughout this article unless otherwise stated.

The XC energy per cell is defined by

\[ E_{\text{XC}} = \int \frac{dx}{a} \int dy \int dz f_{\text{XC}}(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\alpha\beta}, \gamma_{\beta\beta}), \]

where \( \rho \)'s are the electron spin densities and \( \gamma \)'s are the spin density gradient invariants [8]. This integral is usually evaluated by quadrature with Becke’s interlocking multi-atom-centre grid [4] (see also Satoko [5]) as

\[ E_{\text{XC}} \approx \sum_{I} \sum_{g(I)} w_I(r_{g(I)}) f_{\text{XC}}(r_{g(I)}), \]

where \( I \) runs over all atoms in the zeroth cell, \( g(I) \) over all atom-centre grid points of the \( I \)th atom, \( r_{g(I)} \) is the coordinates of the \( g(I) \)th grid point, and \( w_I(r_{g(I)}) \) is the quadrature weight. It should be stressed that the integration domain is always the zeroth cell (although its boundaries are ‘fuzzy’ [4]) and the grid points and weights are defined only within that cell.

Since the XC energy depends on density \( \rho \), atom-centre basis functions, and atom-centre grid, its analytical gradient with respect to a general coordinate \( \xi \) also consists of three terms:

\[ \frac{\partial E_{\text{XC}}}{\partial \xi} = \frac{\partial E_{\text{XC}}}{\partial \xi}^{(b)} + \frac{\partial E_{\text{XC}}}{\partial \xi}^{(d)} + \frac{\partial E_{\text{XC}}}{\partial \xi}^{(q)}. \]

The first term with superscript \( '(b)' \) involves the direct derivatives of the basis functions (not through variation in grid coordinates). The second term with \( '(d)' \) comes from the derivatives of the density matrix elements, which are absorbed in the so-called Pulay force [3]. See Appendix 2 for the first two terms. The third term with \( '(q)' \) is the quadrature derivatives, which consist of the derivatives of grid weights and the derivatives with respect to grid coordinates.

2.1. In-phase atomic gradients

If \( \xi \) is an in-phase atomic coordinate, the sum of the first two terms of Equation (6) (evaluated by the well-known method [6, 8, 12]; see Appendix 2) is nearly equal to the total XC energy gradient [6] for a typical grid size. Small errors due to the neglect of the quadrature derivatives (the third term) are on the order of \( 10^{-5} \) a.u. for a grid used in the preceding energy calculation, which are nevertheless noticeable as a small violation of the translational invariance [8]. The quadrature derivatives erase these small errors and restore the translational invariance at near machine precision (see Section 3).

Taking the \( x \) coordinate of atom \( I \) in the zeroth cell for \( \xi \), the quadrature derivative is written as

\[ \frac{\partial E_{\text{XC}}}{\partial X_{I(0)}}^{(q)} = \sum_{\text{nuc.}} \sum_{g(I)} \frac{\partial w_I(r_{g(I)})}{\partial X_{I(0)}} f_{\text{XC}}(r_{g(I)}), \]

\[ = \sum_{\text{nuc.}} \sum_{g(I)} w_N(r_{g(I)}) \frac{\partial f_{\text{XC}}(r_{g(I)})}{\partial X_{I(0)}} \]

\[ + \sum_{\text{nuc.}} \sum_{g(I)} \frac{\partial w_I(r_{g(I)})}{\partial X_{I(0)}} f_{\text{XC}}(r_{g(I)}) \]

\[ + \sum_{\text{nuc.}} \sum_{g(I)} w_I(r_{g(I)}) \frac{\partial f_{\text{XC}}(r_{g(I)})}{\partial r_{g(I)}} \frac{\partial r_{g(I)}}{\partial X_{I(0)}} \]
The first and second terms in the right-hand sides are, respectively, the derivative of grid weights and the derivative with respect to grid coordinates [6]. They have a large and nearly equal magnitude with opposite signs, cancelling each other nearly exactly. This is why the quadrature derivatives are negligibly small in atomic gradients.

The programmable expression of the first term can be found in Ref. [8]. It is, however, more easily implemented by directly applying the chain rule of differentiation to the code that calculates the quadrature weights. The second term is also easily programmed as a minor modification to the code for \(x\) atomic gradients (see Appendix 2).

### 2.2. Lattice-constant gradient

Next, let us consider the gradient with respect to lattice constant \(a\). Generally, such a gradient should be obtained as a by-product of atomic gradients along \(x\) axis by virtue of the following relationship [15]:

\[
\frac{\partial}{\partial a} = \sum_{n=-S}^{S} \sum_{I} \frac{\partial X_{I(n)}}{\partial a} \frac{\partial}{\partial X_{I(n)}}
\]

\[
= \sum_{n=-S}^{S} \sum_{I} n \frac{\partial}{\partial X_{I(n)}},
\]

where \(n\) runs over the same range of cell indexes adopted for the lattice sums [17] in the preceding energy calculation, \(I\) over all atoms in a cell, and Equation (1) was used. This gives the correct lattice-constant gradient of the HF energy, as pointed out by Teramae et al. [15].

We found [12] that the above formula does not work for the atomic-basis-set DFT. This is because the integration domain of the XC energy depends on \(a\) [see Equation (4)] and the formula ignores such dependence [12]. Instead of Equation (6), we had to begin with the following breakdown of the lattice-constant gradient:

\[
\frac{\partial E_{XC}^{(q)}}{\partial a} = \sum_{I} \sum_{g(I)} \frac{\partial w_I(r_{g(I)})}{\partial a} f_{XC}(r_{g(I)})
\]

\[
+ \sum_{I} \sum_{g(I)} w_I(r_{g(I)}) \frac{\partial f_{XC}(r_{g(I)})}{\partial a} ,
\]

where the last term with superscript ‘(s)’ stands for a surface integral arising from the explicit dependence of the integration domain on \(a\). Specifically, it is the integral of the XC function over the cell boundary at \(x = a\),

\[
\frac{\partial E_{XC}^{(s)}}{\partial a} = \frac{\partial}{\partial a} \int_{0}^{a} dx \int dy \int dz f_{XC}
\]

which is substantial and should not be neglected. In principle, this can be evaluated by two-dimensional quadrature, but we used the following mathematical trick to convert it into a volume integral and evaluated it with the same three-dimensional quadrature of Becke [12]:

\[
\int_0^a dx \int dy \int dz f_{XC}(x = a)
\]

\[
= \int_0^a dx \int dy \frac{xf_{XC}(x = 0, a)}{a}
\]

\[
= \frac{E_{XC}}{a} + \sum_{I} \sum_{g(I)} w_I(r_{g(I)}) X_{g(I)} \frac{\partial f_{XC}(r_{g(I)})}{\partial x} ,
\]

where the penultimate equality used Gauss’ theorem. In this article, we call this term the surface-integral correction, although it is evaluated as the volume integral.

Comparing Equations (6) and (12), we can identify the surface integral with the quadrature derivative (albeit not identically but closely; see Section 3), which is nonvanishing regardless of grid size. The quadrature derivative with respect to \(a\) is written as

\[
\frac{\partial E_{XC}^{(q)}}{\partial a} = \sum_{I} \sum_{g(I)} \frac{\partial w_I(r_{g(I)})}{\partial a} f_{XC}(r_{g(I)})
\]

\[
+ \sum_{I} \sum_{g(I)} w_I(r_{g(I)}) \frac{\partial f_{XC}(r_{g(I)})}{\partial a}
\]

\[
= \sum_{I} \sum_{g(I)} \frac{\partial w_I(r_{g(I)})}{\partial a} f_{XC}(r_{g(I)})
\]

\[
+ \sum_{I} \sum_{g(I)} w_I(r_{g(I)}) \frac{\partial r_{g(I)}}{\partial a} \frac{\partial f_{XC}(r_{g(I)})}{\partial r_{g(I)}}
\]

\[
= \sum_{I} \sum_{g(I)} \frac{\partial w_I(r_{g(I)})}{\partial a} f_{XC}(r_{g(I)}).
\]

Since no grid points in the zeroth cell move with \(a\) (recall \(E_{XC}\) is an integral within the volume of the zeroth cell), the second term (the derivatives with respect to grid coordinates) vanishes identically. The first term survives because Becke’s fuzzy cell weights for grid points in the zeroth cell are influenced by grid points of nearby atoms, which may move with \(a\). Consequently, near exact cancellation of the two terms does not occur in the quadrature derivatives with respect to the lattice constant. The quadrature derivative in the lattice-constant gradient remains large and should not be neglected.
2.3. Helical-angle gradient

Invoking the same strategy embodied by Equation (11), we may be led to an identity,

\[
\frac{\partial \theta}{\partial \vec{r}} = \sum_{n=-S}^{S} \sum_{I} \left\{ \frac{\partial Y_{I(n)}}{\partial \theta} \frac{\partial Y_{I(0)}}{\partial \theta} - \frac{\partial Y_{I(0)}}{\partial \theta} \frac{\partial Y_{I(n)}}{\partial \theta} \right\}
\]

\[
\frac{\partial \theta}{\partial \vec{r}} = \sum_{n=-S}^{S} \sum_{I} \left\{ \frac{\partial Y_{I(n)}}{\partial \theta} \frac{\partial Z_{I(0)}}{\partial \theta} + \frac{\partial Z_{I(n)}}{\partial \theta} \frac{\partial Y_{I(0)}}{\partial \theta} \right\}
\]

\[
\frac{\partial \theta}{\partial \vec{r}} = \sum_{n=-S}^{S} \sum_{I} \left\{ \frac{\partial Z_{I(n)}}{\partial \theta} \frac{\partial Z_{I(0)}}{\partial \theta} + \frac{\partial Z_{I(0)}}{\partial \theta} \frac{\partial Z_{I(n)}}{\partial \theta} \right\}
\]

This appears to suggest that the helical-angle gradient should be obtainable as a by-product of atomic gradi- ents along y and z axes. This turns out to be false even at the HF level. What is erroneously neglected here [but not in Equation (11)] is the fact that the basis functions not only shift their centres but also rotate with the helix (and only with these translating-rotating basis functions does the Bloch theorem hold). See Appendix 2 for the helical-angle gradient formalism that takes into account the quadrature derivatives of atom-centre grids as the quadrature derivative. In this sense, taking into account the quadrature derivatives of atom-centre grids seems to be the most general and reliable method of formulating analytical derivatives even when a different numerical integration method is being employed.

3. Numerical analysis

Some of the B3LYP/6-31G and B3LYP/cc-pVDZ energy gradients [18] of helical polyethylene are given in Tables 1 and 2, respectively. The structure of the helical repeat unit cell, which is a CH₂ unit, along with the lattice constant or ‘rise’ a and helical angle or ‘twist’ θ, are given in Table 3. Note that our B3LYP functional used the VWN5 local correlation functional. The Namur cutoff criterion was adopted with the short-range cutoff of S = 10 and long-range cutoff of L = 30 without a multipole-expansion correction [17]. The number of wave vector (k) sampling points was 100 in the reciprocal unit cell. The integral screening threshold for the two-electron-integral evaluation [19] was \(1 \times 10^{-11}\) a.u. All calculations were performed with the POLYMER programme [20].

The grid is defined only in the zeroth cell and consists of interlocking atom-centre grids [4], each of which is a product of the Gauss–Chebyshev radial grid [4] and Lebedev angular grid [21–26]. Their orientations are fixed in some user-defined coordinates (cf. Equation (5) of Ref. [8]) rather than in the molecular axes (cf. Equation (7) of Ref. [9]), thus making the energy and gradients vary slightly with the user’s arbitrary choice of the coordinates since the Lebedev grids are not rotationally invariant. This orientation-dependence is minimised by inclusion of the quadrature derivatives [9] and eventually eliminated in the limit of an infinitely dense grid. Conclusions of this article are unchanged by the lack of rotational invariance of the grids.
In-phase atomic gradients change noticeably upon inclusion of the quadrature derivatives for the small (25 × 86) grid consisting of 25 radial points × 86 angular points per atom. With increasing grid size, the differences between gradients with and without the quadrature derivatives taper below 2 × 10^{−7} a.u. Concomitantly, the deviations from the translational invariance (the absolute value of the sum of the x atomic gradients) without the quadrature derivatives are on the order of 10^{−4} a.u. or more for the 25 × 86 grid, but they decrease to 10^{−8} a.u. or less for the 300 × 974 grid. With the quadrature derivatives, the deviations become on the order of the integral screening threshold regardless of grid size.

Curiously, the atomic gradients without the quadrature derivatives seem consistently closer to the values in the limit of an infinitely dense grid. However, the atomic
Table 3. The Cartesian coordinates (in bohr) of atoms, the lattice constant or ‘rise’ \( a \) (in bohr), and the helical angle or ‘twist’ \( \theta \) (in degrees) of the \( CH_2 \) repeat unit in helical polyethylene.

| \( x \) | \( y \) | \( z \) |
|---|---|---|
| \( H_1 \) | 0.1 | 2.0 | 1.0 |
| \( C \) | 0.0 | 0.5 | 0.0 |
| \( H_2 \) | 0.0 | 2.0 | −1.0 |
| \( a \) | 2.5 |
| \( \theta \) | 170.0 |

gradients with the quadrature derivatives are within \( 1 \times 10^{-7} \) a.u. of the finite-difference benchmarks regardless of grid size, and are, therefore, more precise. With a grid that is sufficiently large for energy calculations (the 8565 or 100 × 302 grid), the differences are negligible for atomic gradients, if not for frequency calculation [9–11].

The lattice-constant gradient without the quadrature derivatives or surface-integral correction differs from the correct value by an order of magnitude and has the wrong sign even for the gigantic 300 × 974 grid. The addition of the surface integral brings it within \( 2 \times 10^{-4} \) a.u. of the correct value for the 25 × 86 grid and within less than \( 10^{-7} \) a.u. for the 300 × 974 grid. On the other hand, the deviations of the lattice-constant gradient with the quadrature derivatives from the finite-difference benchmarks are on the order of \( 10^{-7} \) a.u. for the 8565 or 25 × 86 grid (these slight deviations are due to the finite-difference approximation). The more precise agreement between the latter two methods indicates that the surface integral method is slightly approximate and the method including the quadrature derivatives should always be trusted, although the error in the surface integral is negligible. Not including either the surface-integral correction or quadrature derivatives will lead to unacceptably large errors in the lattice-constant gradient, rendering the method useless.

The helical-angle gradient without the quadrature derivatives is wrong by the same order of magnitude as the gradient itself regardless of grid size for this particular geometry. The value with the quadrature derivatives agrees with the finite-difference benchmark within a few \( 10^{-7} \) a.u. for the 8565 or 25 × 86 grid, and these small errors are ascribed to the finite-difference approximation. It is, therefore, crucial to include the quadrature derivatives in this gradient also.

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Appendices

Appendix 1. Energy of a helical polymer

In atomic units, energy per helical repeat unit cell of an infinitely extended helix is written as

$$E = E_{NR} + E_T + E_{NA} + E_I + cE_K + E_{XC} + E_{MEP},$$  \hspace{1cm} (A1)

which encompasses the spin-restricted HF theory ($c = 1$ and $E_{XC} = 0$) and a pure local or gradient-corrected DFT ($c = 0$ and $E_{XC} \neq 0$) as well as a hybrid DFT such as B3LYP [18] ($c \neq 0$ and $E_{XC} \neq 0$). Generalizing it to the spin-unrestricted case should be straightforward.

The first term is the nuclear-repulsion energy, which is written as

$$E_{NR} = \frac{1}{2} \sum_{n=-L}^{L} \sum_{IJ} \sum_{\mu,\nu} Z_I Z_J \bar{R}_{IJ(n)},$$  \hspace{1cm} (A2)

where $I$ and $J$ run over all nuclei with nuclear charges of $Z_I$ and $Z_J$, and $n$ runs over cells ($-L \leq n \leq L$) with $L$ standing for the long-range lattice sum cutoff [17]. Summands with zero denominator are excluded from the summation. $R_{IJ(n)}$ is the position of the $I$th nucleus in the $n$th cell,

$$R_{IJ(n)} = (X_{I(n)}, Y_{I(n)}, Z_{I(n)}),$$  \hspace{1cm} (A3)

whose elements are defined by Equations (1)–(3). The $n$th cell is twisted anticlockwise by $n\theta$ relative to the zeroth cell.

The second term is the kinetic energy per cell expressed as

$$E_T = \sum_{n=-S}^{S} \sum_{\mu,\nu} \bar{\rho}_{\mu(n)v(n)} \bar{T}_{\mu(n)v(n)},$$  \hspace{1cm} (A4)

where $\bar{T}_{\mu(n)v(n)}$ is the density matrix element (defined at the end of this Appendix) for the $\mu$th contracted Gaussian-type orbital (cgs) in the zeroth cell and the $v$th cgs in the $n$th cell that translates and rotates with the helix (defined in the next paragraph). $S$ is the short-range lattice sum cutoff [17]. $\bar{T}_{\mu(n)v(n)}$ is the corresponding kinetic-energy integral, defined by

$$\bar{T}_{\mu(n)v(n)} = \int dr \chi^*_{\mu(n)}(r) \left(-\frac{1}{2} \nabla^2\right) \chi_{v(n)}(r),$$  \hspace{1cm} (A5)

where $\chi_{v(n)}(r)$ is the translating-rotating $v$th cgs in the $n$th cell. Generally, tilde indicates screw-axis-symmetry-adapted quantities throughout this article.

Specifically, a screw-axis-symmetry-adapted cgs is given as a linear combination of the also screw-axis-symmetry-adapted primitive Gaussian-type orbital (pgs). It is therefore defined by

$$\tilde{\chi}_{\alpha}(r) = \sum_{\mu} \bar{c}_{\alpha \mu} (\tilde{x}_{\mu}(r))^{n_x} (\tilde{y}_{\mu}(r))^{n_y} (\tilde{z}_{\mu}(r))^{n_z} \times \exp\left(-c_{\alpha} |r - R_{\mu(n)}|^2\right),$$  \hspace{1cm} (A6)

where $c_{\alpha}$ is the product of contraction coefficient and normalization factor of the $\alpha$th pgs, $c_{\alpha}$ is the exponent of the $\alpha$th pgs, and $R_{\mu(n)}$ is the coordinates of the nucleus in the $n$th cell on which the $\mu$th cgs and all of its constituent pgs are centred.

The coordinates $\tilde{x}_{\mu}(n)$, $\tilde{y}_{\mu}(n)$, $\tilde{z}_{\mu}(n)$ are the $n$th-cell-fixed Cartesian coordinates that rotate with the helix and are centred on $R_{\mu(n)} = (X_{\mu(n)}, Y_{\mu(n)}, Z_{\mu(n)})$. They are related to the space-fixed Cartesian coordinates $r = (x, y, z)$ by

$$\tilde{x}_{\mu}(n) = x - X_{\mu(n)} = x - na - X_{\mu(0)},$$  \hspace{1cm} (A7)
$$\tilde{y}_{\mu}(n) = (y - Y_{\mu(n)}) \cos n\theta + (z - Z_{\mu(n)}) \sin n\theta = y \cos n\theta + z \sin n\theta - Y_{\mu(0)},$$  \hspace{1cm} (A8)
$$\tilde{z}_{\mu}(n) = -(y - Y_{\mu(n)}) \sin n\theta + (z - Z_{\mu(n)}) \cos n\theta = -y \sin n\theta + z \cos n\theta - Z_{\mu(0)}.$$

Only with these screw-axis-symmetry-adapted (i.e. translating-rotating) basis functions does the Bloch theorem [27] hold, guaranteeing the translational invariance of matrices with tilde:

$$\bar{T}_{\mu(n)v(n)} = \bar{T}_{\mu(0)v(n-m)},$$  \hspace{1cm} (A10)
$$\bar{\rho}_{\mu(n)v(n)} = \bar{\rho}_{\mu(0)v(n-m)}. $$  \hspace{1cm} (A11)

However, various molecular integrals are more conveniently evaluated [19] for cgs in the space-fixed Cartesian coordinates without tilde:

$$\chi_{\alpha}(r) = \sum_{\mu} c_{\alpha \mu} (x - X_{\mu(0)})^{n_x} (y - Y_{\mu(0)})^{n_y} (z - Z_{\mu(0)})^{n_z} \times \exp\left(-c_{\alpha} |r - R_{\mu(0)}|^2\right).$$  \hspace{1cm} (A12)

The kinetic-energy-integral matrix in these non-symmetry-adapted cgs is defined by and computed as

$$T_{\mu(0)v(n)} = \int dr \bar{\rho}_{\mu(0)v(n)} \left(-\frac{1}{2} \nabla^2\right) \chi_{v(n)}(r),$$  \hspace{1cm} (A13)

using the standard algorithms such as the Obara–Saika method [19]. Generally, quantities without tilde designate those in the basis of the space-fixed Cartesian coordinates in this article.

The screw-axis-symmetry-adapted kinetic-energy integrals are obtained from the non-symmetry-adapted ones by the transformation

$$\bar{T}_{\mu(n)v(n)} = \sum_{\nu} T_{\mu(0)v(n)} R_{\nu(0)}(n) T_{\mu(0)v(n)},$$  \hspace{1cm} (A14)

where $R_{\nu(0)}(n)$ is the rotation matrix for the $n$th cell. The latter is a unit matrix in which the 3-by-3 block in a normalised $p$ subshell (ordered $p_x, p_y, p_z$) is replaced by

$$R_{\nu(0)}(n) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & c & s \\ 0 & -s & c \end{pmatrix},$$  \hspace{1cm} (A15)

with $c = \cos n\theta$ and $s = \sin n\theta$, the 6-by-6 block in a normalised Cartesian $d$ subshell (ordered $d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{yz}, d_{zx}$)
The third term of Equation (A1) is the nuclear-attraction energy given by

\[ E_{\text{NA}} = \sum_{n=-S}^{S} \sum_{\mu,\nu} c_{\text{gs}} P_{\mu(0)\nu(n)} \tilde{N}_{\mu(0)\nu(n)}. \]  

where the so-called \( J \) and \( K \) integrals in the translating-rotating basis functions are obtained by the same transformation,

\[ \tilde{J}_{\mu(0)\nu(n)} = \sum_{\nu'} c_{\text{gs}} R_{\nu'\nu(0)} I_{\mu(0)\nu'(n)}, \]  
\[ \tilde{K}_{\mu(0)\nu(n)} = \sum_{\nu'} c_{\text{gs}} R_{\nu'\nu(0)} K_{\mu(0)\nu'(n)}. \]

The and \( K \) integrals in the space-fixed Cartesian coordinates are, in turn, built from two-electron integrals:

\[ J_{\mu(0)\nu(n)} = \sum_{l=-L}^{L} \sum_{m=-S}^{S} \sum_{\kappa,\lambda} P_{\kappa(\lambda)\lambda(l+m)} \times \langle \mu(0)v(n) | \kappa(l)\lambda(l + m) \rangle, \]  
\[ K_{\mu(0)\lambda(m)} = -\frac{1}{2} \sum_{l=-L}^{L} \sum_{n=-S}^{S} \sum_{\kappa,\nu} c_{\text{gs}} P_{\kappa(\nu)(\mu)(0)v(n)} \times \langle \kappa(l)\lambda(m) \rangle, \]

with

\[ \langle \mu(0)v(n) | \kappa(l)\lambda(l + m) \rangle = \int \frac{dr_{1}dr_{2}}{r_{1}r_{2}} \chi_{\mu(0)}^{*}(r_{1}) \chi_{\nu(0)}(r_{2}) \times \frac{1}{r_{1}r_{2}} \gamma_{\nu(0)}(r_{2}) \chi_{\lambda(l + m)}(r_{2}), \]

in the Mulliken notation. The density matrix in the space-fixed Cartesian coordinates entering the above equations is obtained by the back-transformation,

\[ P_{\mu'(0)v'(m)} = \sum_{\mu',\nu'} c_{\text{gs}} P_{\mu'(0)v'(m-l)} \tilde{R}_{\nu'(\mu')(l)} \tilde{R}_{\nu'\nu(m)}, \]

which is no longer expected to possess the translational invariance, i.e.

\[ P_{\mu(0)v(n)} \neq P_{\mu(0)v(-n)}. \]

The penultimate term of Equation (A1), \( E_{\text{XC}} \), is the exchange-correlation (XC) energy evaluated by quadrature [see Equation (5)]. Integrand \( f_{\text{XC}} \) has the same screw-axis symmetry as the helix and so the XC energy per cell can be evaluated as its integral over the zeroth cell volume. In practice, an infinitely extended \( f_{\text{XC}} \) is divided into cellwise contributions in a gradually overlapping manner by Becke’s fuzzy cell scheme.

The electron density and density gradient invariant are defined only within the zeroth cell (where the space-fixed and translating-rotating Cartesian coordinates coincide) and evaluated explicitly with the translating-rotating basis functions.

\[ \rho(r) = \sum_{m, n=-S}^{S} \sum_{\mu, \nu} c_{\text{gs}} \tilde{P}_{\mu(0)v(n)} \tilde{\gamma}_{\mu(0)v(n)}(r), \]  
\[ \gamma(r) = \nabla \rho(r) \cdot \nabla \rho(r) \]

with

\[ \frac{\partial \rho(r)}{\partial x} = \sum_{m, n=-S}^{S} \sum_{\mu, \nu} c_{\text{gs}} \tilde{P}_{\mu(0)v(n)} \tilde{\gamma}_{\mu(0)v(n)}(r) \frac{\partial \chi_{\mu(0)v(n)}(r)}{\partial x}. \]
where Equation (A7) was used, and
\[
\frac{\partial \rho(r)}{\partial y} = \sum_{m, n = -S}^{S} \sum_{\mu, \nu} \bar{p}_{\mu(n)} \frac{\partial \tilde{x}_{\mu}(r)}{\partial y} \tilde{x}_{\nu}(m) + \sum_{m, n = -S}^{S} \sum_{\mu, \nu} \bar{p}_{\mu(n)} \frac{\partial \tilde{x}_{\mu}(r)}{\partial y} \tilde{x}_{\nu}(m) \cos m \theta + \sum_{m, n = -S}^{S} \sum_{\mu, \nu} \bar{p}_{\mu(n)} \frac{\partial \tilde{x}_{\mu}(r)}{\partial y} \tilde{x}_{\nu}(m) \sin m \theta,
\]  
(A32)

as well as
\[
\frac{\partial \rho(r)}{\partial z} = \sum_{m, n = -S}^{S} \sum_{\mu, \nu} \bar{p}_{\mu(n)} \frac{\partial \tilde{x}_{\mu}(r)}{\partial z} \tilde{x}_{\nu}(m) + \sum_{m, n = -S}^{S} \sum_{\mu, \nu} \bar{p}_{\mu(n)} \frac{\partial \tilde{x}_{\mu}(r)}{\partial z} \tilde{x}_{\nu}(m) \cos m \theta + \sum_{m, n = -S}^{S} \sum_{\mu, \nu} \bar{p}_{\mu(n)} \frac{\partial \tilde{x}_{\mu}(r)}{\partial z} \tilde{x}_{\nu}(m) \sin m \theta,
\]  
(A33)

where Equations (A8) and (A9) were used.

The XC integrals, necessary in the self-consistent field procedure (see below), are also evaluated by quadrature.
\[
\tilde{x}_{\mu(n)} = \int dr \tilde{x}_{\mu(n)} \tilde{x}_{\nu}(n) + 2 \int dr \tilde{x}_{\mu(n)} u_{\nu}(r) \nabla \rho(r) \cdot \nabla \tilde{x}_{\nu}(n) + 2 \int dr \nabla \tilde{x}_{\mu(n)} \cdot \nabla \rho(r) u_{\nu}(r) \tilde{x}_{\nu}(n)
\]  
(A35)

\[
\approx \sum_{m, n = -S}^{S} \sum_{I} w_{I(r(n))} \tilde{x}_{\mu(n)} \tilde{x}_{\nu}(m) \tilde{x}_{\nu}(n)
\]  
(A36)

where the XC potentials are defined only within the zeroth cell as
\[
v_{\text{XC}}(r) = \frac{\partial f_{\text{XC}}(r)}{\partial \rho(r)},
\]  
(A37)

\[
u_{\text{XC}}(r) = 1 \frac{\partial f_{\text{XC}}(r)}{\partial \rho(r)} + 4 \frac{\partial f_{\text{XC}}(r)}{\partial \gamma_{ao}(r)}
\]  
(A38)

The derivatives of the translating-rotating basis functions with respect to the space-fixed Cartesian coordinates are evaluated as
\[
\frac{\partial \tilde{x}_{\nu}(n)}{\partial x} = \frac{\partial \tilde{x}_{\nu}(n)}{\partial \tilde{x}_{\nu}(n)}
\]  
(A39)

\[
\frac{\partial \tilde{x}_{\nu}(n)}{\partial y} = \frac{\partial \tilde{x}_{\nu}(n)}{\partial \tilde{x}_{\nu}(n)} \cos m \theta - \frac{\partial \tilde{x}_{\nu}(n)}{\partial \tilde{x}_{\nu}(n)} \sin m \theta
\]  
(A40)

\[
\frac{\partial \tilde{x}_{\nu}(n)}{\partial z} = \frac{\partial \tilde{x}_{\nu}(n)}{\partial \tilde{x}_{\nu}(n)} \sin m \theta + \frac{\partial \tilde{x}_{\nu}(n)}{\partial \tilde{x}_{\nu}(n)} \cos m \theta
\]  
(A41)

The derivatives on the right-hand sides are computed on each grid point explicitly.

In Equations (A30)–(A36), two translating-rotating basis functions are generally centred in different cells, while \(v_{\text{XC}}\) is infinitely extended and periodic. Therefore, in principle, one needs to integrate the respective functions in all cells, using grid that is translated and rotated along the helix. An equivalent integration is achieved by defining grid only within the zeroth cell and translate and rotate the two basis functions along the helix. We have chosen the latter method and the above equations reflect this choice.

The last term, \(E_{\text{MPE}}\), stands for the multipole-expansion correction [17]. In the leading order, it is given by
\[
E_{\text{MPE}} = \sum_{n=L+1}^{\infty} \frac{1}{(n+3)^4} \left( -2 \mu_x^2 + \mu_y^2 \cos n \theta + \mu_z^2 \cos n \theta \right)
\]  
(A42)

where \((\mu_x, \mu_y, \mu_z)\) is related to the zeroth cell dipole moment, and \(\infty\) is mimicked by a large integer (10,000 in our implementation). Note that the charge-quadruple interactions, which also decay as \(r^{-3}\) and were recommended for inclusion by Delhalle et al. [17], are excluded in this study, so that the energy is variational and consistent with the analytical gradients (see Appendix 2). The corresponding correction to the Kohn–Sham Hamiltonian (or Fock) matrix elements are
\[
\hat{M}_{\mu(n)} = \sum_{v} R_{\mu(n)} \mu_{\nu}(n)
\]  
(A43)
with

\[ M_{\mu(0)v(n)} = \sum_{m=L+1}^{\infty} \frac{1}{(ma)^3} \left\{ -4x_{\mu(0)v(n)} \mu_x + 2y_{\mu(0)v(n)} \mu_y \cos \theta b + 2z_{\mu(0)v(n)} \mu_z \cos \theta b \right\} \]

Integrals \( x_{\mu(0)v(n)} \), \( y_{\mu(0)v(n)} \), and \( z_{\mu(0)v(n)} \) are the moment integrals of the space-fixed Cartesian coordinates in the nonrotating basis functions. For instance, a \( y \) moment integral is defined by and evaluated as

\[ y_{\mu(0)v(n)} = \int dr \, \chi_{\mu(0)}^*(r) y \chi_{\nu(n)}(r), \quad (A45) \]

which, in turn, gives the \( y \) 'dipole moment' for the zeroth cell as

\[ \mu_y = \sum_{n=-S}^{S} \sum_{\nu} c_{\mu n}^* y_{\mu(0)v(n)} - \mu_{\text{nucl}} \sum_{\nu} Z_y y_1, \quad (A46) \]

where the density matrix in the space-fixed Cartesian coordinates is given by Equation (A28).

The Kohn–Sham Hamiltonian (or Fock) and overlap matrices in the translating-rotating basis functions are defined by

\[ \tilde{F}_{\mu(0)v(n)} = T_{\mu(0)v(n)} + \tilde{N}_{\mu(0)v(n)} + \tilde{J}_{\mu(0)v(n)} + c\tilde{K}_{\mu(0)v(n)} + \tilde{X}_{\mu(0)v(n)} + \tilde{M}_{\mu(0)v(n)}, \quad (A47) \]

and

\[ \tilde{S}_{\mu(0)v(n)} = \sum_{\nu'} R_{\mu v'}(n) S_{\mu(0)v'(n)}, \quad (A48) \]

with

\[ S_{\mu(0)v(n)} = \int dr \, \chi_{\mu(0)}^*(r) \chi_{\nu(n)}(r). \quad (A49) \]

The dynamical Fock and overlap matrices are then constructed as

\[ \tilde{F}_{\mu v}(k) = \sum_{n=-S}^{S} \tilde{F}_{\mu(0)v(n)} \exp(inka), \quad (A50) \]

\[ \tilde{S}_{\mu v}(k) = \sum_{n=-S}^{S} \tilde{S}_{\mu(0)v(n)} \exp(inka), \quad (A51) \]

where \( k \) is the wave vector \((-\pi/a \leq k < \pi/a)\). At this point, the dynamical matrices in the spherical \( d \) and \( f \) translating-rotating basis functions (if applicable) can be obtained by the transformations,

\[ \tilde{F}_{\mu v}(k) = \sum_{\mu',v'} cgs Q_{\mu' v'} \tilde{F}_{\mu' v'}(k), \quad (A52) \]

\[ \tilde{S}_{\mu v}(k) = \sum_{\mu',v'} cgs Q_{\mu' v'} \tilde{S}_{\mu' v'}(k), \quad (A53) \]

The transformation matrix is a unit matrix in which the 6-by-6 block in a normalised Cartesian \( d \) subshell (in the same order as before) is replaced by

\[ Q_{\mu' v'}(n) = \begin{pmatrix} \sqrt{3/2} & -\sqrt{3/2} & 0 & 0 & 0 & 0 \\ -1/2 & -1/2 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad (A54) \]

or the 10-by-10 block in a normalised Cartesian \( f \) subshell (in the same order as before) is swapped by

\[ Q_{\mu' v'}(n) = \begin{pmatrix} 0 & 0 & 1 & 0 & -3\sqrt{3}/10 \\ -\sqrt{3}/4 & 0 & 0 & 0 & 0 \\ -\sqrt{3}/4 & 0 & -\sqrt{30}/20 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \sqrt{30}/5 & -\sqrt{30}/20 & 0 & 0 & 0 \\ -3\sqrt{3}/4 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \]

\[ \tilde{C}_{d}(k) = \sum_{v} \tilde{C}_{d v'}(k) Q_{v' v} \]

\[ \tilde{C}_{f}(k) = \sum_{v} \tilde{C}_{f v'}(k) Q_{v' v} \]

\[ \tilde{C}_{d}(k) = \sum_{v} \tilde{C}_{d v'}(k) Q_{v' v} \]

The density matrix in the Cartesian \( d \) and \( f \) translating-rotating basis functions is then given by

\[ \tilde{P}_{\mu(0)v(m)} = \frac{2}{K} \sum_{m} \sum_{k} f_{m}(k) \bar{C}_{\mu v}(k) \tilde{C}_{d v'}(k) \exp(inka), \quad (A58) \]

with \( f_{m}(k) \) being the Fermi–Dirac distribution function,

\[ f_{m}(k) = \frac{1}{\exp[\beta(\epsilon_{m}(k) - \epsilon_f)] + 1}. \quad (A59) \]
where $\beta = (k_B T)^{-1}$ and the Fermi energy $\epsilon_F$ is determined by the electro-neutrality condition:

$$\sum_l Z_l = \sum_{n=-S}^S \sum_{\mu, \nu} \tilde{P}_\mu(n) \delta_{\mu(0)}(n).$$  \hspace{1cm} (A60)

### Appendix 2. Energy gradients of a helical polymer with respect to the helical angle $\theta$

We shall consider the gradient of the total energy per cell with respect to the helical angle $\theta$ as the most complex example:

$$\frac{\partial E}{\partial \theta} = \frac{\partial E^{(h)}}{\partial \theta} + \frac{\partial E^{(d)}}{\partial \theta} + \frac{\partial E^{(q)}}{\partial \theta} + \frac{\partial E^{(q)}}{\partial \theta}.$$  \hspace{1cm} (A61)

Gradients with respect to the in-phase atomic coordinates $X_\ell(0)$, $Y_\ell(0)$, $Z_\ell(0)$, or to the lattice constant $a$ can be inferred from it. The first term in the right-hand side of the above equation is the Hellmann–Feynman force, the second term has to do with the derivatives of basis functions (not through grid coordinates), the third term the density matrix derivatives, and the fourth term the quadrature derivatives.

The Hellmann–Feynman force consists of two terms:

$$\frac{\partial E^{(h)}}{\partial \theta} = \frac{\partial E_{NR}}{\partial \theta} + \frac{\partial E_{NA}}{\partial \theta},$$  \hspace{1cm} (A62)

each of which is easily formulated and will not be repeated here. The density matrix derivatives are consolidated into the so-called Pulay force by virtue of the variational nature of the HF or DFT energy. It is given by

$$\frac{\partial E^{(d)}}{\partial \theta} = -\sum_{n=-S}^S \sum_{\mu, \nu} \tilde{W}_\mu(n) \tilde{S}_{\mu(0)}(n) \frac{\partial S_{\mu(0)}}{\partial \theta},$$  \hspace{1cm} (A63)

with the energy-weighted density matrix,

$$\tilde{W}_\mu(n) = \frac{2}{K} \sum_m \sum_k f_m(k) \epsilon_m(k) \tilde{C}_\mu(k) \tilde{C}_\nu(k) \exp(inka).$$  \hspace{1cm} (A64)

The quadrature derivatives exist only in the XC energy gradient and are extensively discussed in the main text.

$$\frac{\partial E^{(q)}}{\partial \theta} = \frac{\partial E_{XC}}{\partial \theta}.$$  \hspace{1cm} (A65)

Therefore, in the remainder of this Appendix, we shall focus on the basis function derivatives:

$$\frac{\partial E^{(b)}}{\partial \theta} = \frac{\partial E^{(b)}}{\partial \theta} + \frac{\partial E_{NA}}{\partial \theta} + \frac{\partial E^{(b)}}{\partial \theta} + \frac{\partial E_{E}}{\partial \theta} + \frac{\partial E^{(b)}}{\partial \theta} + \frac{\partial E_{MPD}}{\partial \theta}.$$  \hspace{1cm} (A66)

The basis function derivative of the kinetic energy with respect to $\theta$ is given by

$$\frac{\partial E_T^{(b)}}{\partial \theta} = \sum_{n=-S}^S \sum_{\mu, \nu} \tilde{P}_\mu(n) \delta_{\mu(0)}(n) \frac{\partial T_{\mu(0)}}{\partial \theta}.$$  \hspace{1cm} (A67)

In the last expression, the first term accounts for the basis function rotation, while the second for the basis function centre shift. Equation (22) is wrong for it neglects the first term. The derivative of the kinetic-energy integral in the space-fixed Cartesian coordinates with respect to $\theta$ is computed as

$$\frac{\partial T_{\mu(0)}}{\partial \theta} = \int dr \chi^{*}_{\mu}(r) \left( -\frac{1}{2} \nabla^2 \chi_{\nu}(r) \right) \frac{\partial \chi_{\nu}(r)}{\partial \theta}.$$  \hspace{1cm} (A70)

Here we used the fact that the basis functions in the space-fixed Cartesian coordinates depend only through their centres and that $\partial / \partial V = -\partial / \partial Y$, etc. The molecular integral derivatives appearing in the last expression are evaluated by the standard method [19]. The corresponding derivatives of $\tilde{S}_{\mu(0)}(n)$ and $\tilde{N}_{\mu(0)}(n)$ are obtained in the same way.

The basis function derivative of the Coulomb energy is given by

$$\frac{\partial E_{C}}{\partial \theta} = \frac{1}{2} \sum_{l=-L}^{L} \sum_{n=-S}^{S} \sum_{\mu, \nu, \lambda} \frac{\partial P_{\mu(0)}(m)}{\partial \theta} \left[ P_{\mu(0)}(n) P_{\lambda}(l + m) \right]$$  \hspace{1cm} (A73)

where we used the fact that the basis functions in the space-fixed Cartesian coordinates depend only through their centres and that $\partial / \partial V = -\partial / \partial Y$, etc. The molecular integral derivatives appearing in the last expression are evaluated by the standard method [19]. The corresponding derivatives of $\tilde{S}_{\mu(0)}(n)$ and $\tilde{N}_{\mu(0)}(n)$ are obtained in the same way.

The basis function derivative of the Coulomb energy is given by

$$\frac{\partial E_{C}}{\partial \theta} = \frac{1}{2} \sum_{l=-L}^{L} \sum_{n=-S}^{S} \sum_{\mu, \nu, \lambda} \frac{\partial P_{\mu(0)}(m)}{\partial \theta} \left[ P_{\mu(0)}(n) P_{\lambda}(l + m) \right]$$  \hspace{1cm} (A73)

where we used the fact that the basis functions in the space-fixed Cartesian coordinates depend only through their centres and that $\partial / \partial V = -\partial / \partial Y$, etc. The molecular integral derivatives appearing in the last expression are evaluated by the standard method [19]. The corresponding derivatives of $\tilde{S}_{\mu(0)}(n)$ and $\tilde{N}_{\mu(0)}(n)$ are obtained in the same way.
\[ \frac{\partial}{\partial \theta} (\mu(0) v(n) \mid \kappa(l) \lambda(l + m) ) \] 

The basis function derivative explicitly neglects the variation of density matrix elements. Hence, what is meant by the basis function derivative of the density matrix in the space-fixed Cartesian coordinates is as follows:

\[ \frac{\partial \rho}{\partial \theta} = \sum_{\kappa, \lambda, \lambda'} \hat{P}_{\kappa(0) \lambda(0) \lambda'(m)} \frac{\partial \hat{R}_{\kappa' \lambda'}(l)}{\partial \theta} R_{\kappa \lambda} \hat{I}(l + m) \]

which includes only the effects of basis function rotations on the density matrix, but not the change in the density matrix \((\hat{P})\) itself. The derivative of a two-electron integral with respect to \(\theta\) is given by

\[ \frac{\partial}{\partial \theta} (\mu(0) v(n) \mid \kappa(l) \lambda(l + m) ) \]

\[ = (-n Y_{\kappa(0)} \sin n \theta - n Z_{\kappa(0)} \cos n \theta) \]

\[ \times \left( \mu(0) \left( -\frac{\partial v(n)}{\partial y} \right) \mid \kappa(l) \lambda(l + m) \right) \]

\[ + (n Y_{\kappa(0)} \cos n \theta - n Z_{\kappa(0)} \sin n \theta) \]

\[ \times \left( \mu(0) \left( -\frac{\partial v(n)}{\partial z} \right) \mid \kappa(l) \lambda(l + m) \right) \]

\[ + \left[ (-l + m) Y_{\kappa(0)} \sin(l + m) \theta \right. \]

\[ - (l + m) Z_{\kappa(0)} \cos(l + m) \theta \]

\[ \times \left( \mu(0) v(n) \mid \kappa(l) \left( -\frac{\partial \lambda(l + m)}{\partial y} \right) \right) \]

\[ + \left[ (l + m) Y_{\kappa(0)} \cos(l + m) \theta \right. \]

\[ - (l + m) Z_{\kappa(0)} \sin(l + m) \theta \]

\[ \times \left( \mu(0) v(n) \mid \kappa(l) \left( -\frac{\partial \lambda(l + m)}{\partial z} \right) \right) \].

The corresponding derivative of the exchange energy can be obtained in the same way.

The basis function derivative of the XC energy reads

\[ \frac{\partial E_{\text{XC}}}{\partial \theta} = \frac{\partial}{\partial \theta} \sum_{l, g(l)} w_l (r_{g(l)}) f_{\text{XC}}(r_{g(l)}) \]

\[ = \sum_{l, g(l)} w_l (r_{g(l)}) \frac{\partial f_{\text{XC}}(r_{g(l)})}{\partial \theta} \]

\[ = \sum_{l, g(l)} w_l (r_{g(l)}) \frac{\partial \hat{f}_{\text{XC}}(r_{g(l)})}{\partial \theta} \]

\[ = \sum_{l, g(l)} w_l (r_{g(l)}) \frac{\partial \hat{f}_{\text{XC}}(r_{g(l)})}{\partial \theta} \]
\[
\frac{\partial^2 \rho(r)}{\partial \theta \partial z} = \sum_{m,n=-S}^S \sum_{\mu,\nu} \rho^{(\mu)}(r) \chi^{\ast}_{\mu(n)}(r) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial z} + \sum_{m,n=-S}^S \sum_{\mu,\nu} \rho^{(\mu)}(r) \chi^{\ast}_{\mu(n)}(r) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial z} + \sum_{m,n=-S}^S \sum_{\mu,\nu} \rho^{(\mu)}(r) \chi^{\ast}_{\mu(n)}(r) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial z}.
\]

(A85)

The first derivatives of the translating-rotating basis functions are given by Equations (A39)–(A41) as well as by Equation (A81), which are the equations actually programmed. The second derivatives are then evaluated as

\[
\frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \chi(n)} = \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \chi(n)},
\]

(A86)

\[
\frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \gamma(n)} = \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \gamma(n)} \cos n\theta - \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \gamma(n)} \sin n\theta - \frac{\partial \chi_{\mu(n)}(r)}{\partial \gamma(n)} n \sin n\theta + \frac{\partial \chi_{\mu(n)}(r)}{\partial \gamma(n)} n \cos n\theta,
\]

(A87)

\[
\frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \delta(n)} = \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \delta(n)} \sin n\theta + \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \delta(n)} \cos n\theta + \frac{\partial \chi_{\mu(n)}(r)}{\partial \delta(n)} n \cos n\theta - \frac{\partial \chi_{\mu(n)}(r)}{\partial \delta(n)} n \sin n\theta,
\]

(A88)

where Equations (A7)–(A9) were used. The second derivatives in the right-hand sides are, in turn, given by

\[
\frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \chi(n)} = n \left( -y \sin n\theta + z \cos n\theta \right) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \chi(n) \partial \gamma(n)} + n \left( -y \cos n\theta - z \sin n\theta \right) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \chi(n) \partial \delta(n)},
\]

(A89)

\[
\frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \gamma(n)} = n \left( -y \sin n\theta + z \cos n\theta \right) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \gamma(n) \partial \delta(n)} + n \left( -y \cos n\theta - z \sin n\theta \right) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \gamma(n) \partial \delta(n)},
\]

(A90)

\[
\frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \theta \partial \delta(n)} = n \left( -y \sin n\theta + z \cos n\theta \right) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \delta(n) \partial \gamma(n)} + n \left( -y \cos n\theta - z \sin n\theta \right) \frac{\partial^2 \chi_{\mu(n)}(r)}{\partial \delta(n) \partial \gamma(n)}.
\]

(A91)

The second derivatives appearing on the right-hand sides of these equations are computed explicitly.

The basis function derivative of the multipole-expansion correction is

\[
\frac{\partial E_{\text{MPE}}}{\partial \theta} = \sum_{n=L+1}^{\infty} \frac{1}{(na)^3} \left\{ -4\mu_x \frac{\partial \chi_x}{\partial \theta} + 2\mu_y \frac{\partial \chi_y}{\partial \theta} \cos n\theta + 2\mu_z \frac{\partial \chi_z}{\partial \theta} \cos n\theta - \frac{\partial \chi_x}{\partial \theta} n \sin n\theta \right\},
\]

(A92)

The derivative of the y’ dipole moment’ is then given by

\[
\frac{\partial \mu_y}{\partial \theta} = \sum_{\mu,\nu} \sum_{n=-S}^S \left\{ \rho^{(\mu)}(r) \chi^{\ast}_{\mu(n)}(r) y^{(\nu)(n)} \right\},
\]

(A93)

where the derivative factor in the first term is given by Equation (A75) and the derivative factor in the second term by

\[
\frac{\partial y^{(\nu)}(n)}{\partial \theta} = \int dr \chi^{\ast}_{\mu(0)}(r) y \frac{\partial \chi_{\nu(n)}(r)}{\partial \theta}
\]

\[
= \int dr \chi^{\ast}_{\mu(0)}(r) y \left( -\frac{\partial \chi_{\nu(n)}(r)}{\partial y} \right)
\]

\[
\times \left\{ \frac{\partial Y_{\nu(0)}(r) \chi_{\nu(n)}(r)}{\partial \theta} + \frac{\partial Z_{\nu(0)}(r) \chi_{\nu(n)}(r)}{\partial \theta} \right\}
\]

\[
= (-nY_{\nu(0)}(r) \sin n\theta - nZ_{\nu(0)}(r) \cos n\theta)
\]

\[
\times \int dr \chi^{\ast}_{\mu(0)}(r) y \left( -\frac{\partial \chi_{\nu(n)}(r)}{\partial y} \right)
\]

\[
+ (nY_{\nu(0)}(r) \cos n\theta - nZ_{\nu(0)}(r) \sin n\theta)
\]

\[
\times \int dr \chi^{\ast}_{\mu(0)}(r) y \left( -\frac{\partial \chi_{\nu(n)}(r)}{\partial z} \right).
\]

(A95)

(A96)

It should be cautioned that these dipole derivatives would not agree with the numerical derivatives because the density matrix derivatives are not included in the former; Recall that Equation (A75) only accounts for the effects of basis function rotations on the density matrix. Nevertheless, the total gradients are correct by virtue of the Pulay force [Equation (A63)] that properly takes into account the derivatives of the density matrix elements.