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OBTAINING IONIC FORCES BY THE TOTAL-ENERGY TIGHT-BINDING METHOD

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Abstract: Applying a non-orthogonal tight-binding method to calculate ionic forces in a molecular-dynamics simulation vastly improves the transferability the model's transferability to different environments, compared with the traditional empirical potential-driven molecular-dynamics. In this paper we present the details of computing derivatives of Hamiltonian and overlap matrix elements appearing in the Hellmann-Feynman expression for ionic forces in the NRL-TB model of tight-binding. The presented expressions are validated with the results obtained using a tight-binding-driven molecular-dynamics program.

Keywords: total-energy tight-binding, TBMD, Hellmann-Feynman, ionic forces, molecular-dynamics

1. Introduction

The molecular-dynamics (MD) method is a powerful simulation tool of usefulness proven over the last thirty years. However, its traditional formulation, in which empirical potentials are used to drive the system, suffers from well-known limitations. Since the parameters of the potential are usually fitted to reproduce the bulk properties of material under study, the model behaves poorly when applied to systems considerably far from the bulk structure. Assuming a particular functional form for the potential and neglecting the electronic structure altogether is another factor accounting for the poor transferability of empirical potential-driven MD.

To allay these difficulties one can explicitly include electrons in the picture and extract ionic forces using a quantum mechanics-based MD formulation. One of the computationally cheapest approaches, which still manages to qualitatively capture the relevant electronic effects uses the tight-binding (TB) method. NRL-TB, or total-energy tight-binding, is one of the more successful TB variants, offering substantial transferability and ready-to-use parametrizations for a wide spectrum of elements [1–5].

2. Obtaining ionic forces by the NRL-TB total-energy method

In the non-orthogonal tight-binding formulation, the Schrödinger equation is solved by expanding the one-electron wavefunction Ψ_n as a linear combination of atomic orbitals $\phi_{i,\alpha}$ centered on all atoms i:

$$\Psi_n = \sum_{i,\alpha} c^n_{i,\alpha} \phi_{i,\alpha}, \tag{1}$$

with α describing the symmetry of the basis functions. In the sp^3d^5 model typically used for d-band metals, $\alpha \in \{s, x, y, z, xy, yz, zx, x^2-y^2, 3z^2-r^2\}$.

The Hamiltonian and overlap operators are thus replaced by a Hamiltonian matrix, $\mathcal{H}$, and an overlap matrix, $\mathcal{S}$, and the secular equation,

$$\mathcal{H}\mathcal{C} = \varepsilon \mathcal{S}\mathcal{C}, \tag{2}$$

is solved for eigenenergies $\boldsymbol{\varepsilon} = \{\varepsilon_n\}$ and expansion coefficients $\mathcal{C} = \{c^n_{i,\alpha}\}$.

In the NRL-TB formulation [1–5], the on-site terms for atom i depend on its associated local density, ϱ_i, and are of the following form:

$$\mathcal{H}_{i\alpha,i\alpha} = \langle \phi_{i,\alpha} | \hat{H} | \phi_{i,\alpha} \rangle = a_q + b_q \varrho_i^{2/3} + c_q \varrho_i^{4/3} + d_q \varrho_i^2, \tag{3}$$

where i denotes the atom's number and a_q, b_q, c_q and d_q, with $q \in \{s, p, d\}$, act as parameters. The local density at atom i, ϱ_i, is defined as:

$$\varrho_i = \sum_{j \neq i} \exp(-\lambda^2 R_{ij}) F_c(R_{ij}), \tag{4}$$

where λ is a parameter, R_{ij} is the Cartesian distance between atoms i and j, and $F_c(\cdot)$ is a cutoff function of the following form:

$$F_c(R) = \frac{\Theta(R_c - R)}{1 + \exp\big((R - R_c)/\ell\big) + 5}, \tag{5}$$

where Θ is the step function, ℓ is a constant and R_c denotes the cutoff radius, beyond which the function vanishes. The non-diagonal on-site elements (*i.e.* $\mathcal{H}_{i\alpha,i\beta}$, $\alpha \neq \beta$) are assumed to be zero.

The NRL-TB method employs the two-centre approximation for the off-site elements of the Hamiltonian, $\mathcal{H}_{i\alpha,j\beta} = \langle \phi_{i,\alpha} | \hat{H} | \phi_{j,\beta} \rangle$, $j \neq i$. These terms are linear combinations of up to three two-center integrals, $H_\gamma(R)$, $\gamma \in \{ss\sigma, sp\sigma, pp\sigma, pp\pi, sd\sigma, pd\sigma, pd\pi, dd\sigma, dd\pi, dd\delta\}$, with the combination's coefficients, $\Phi_{\alpha\beta}(l,m,n)$, describing the angular momentum dependence of the orbital interactions in terms of the direction cosines l, m, n of the vector between atoms i and j. We thus have:

$$\mathcal{H}_{i\alpha,j\beta} = \sum_{s=1}^{3} \Phi_{s,\alpha\beta}(l,m,n) H_{\gamma_s}(R_{ij}). \tag{6}$$

The original paper of Slater and Koster [6] gives the expansion of $\mathcal{H}_{i\alpha,j\beta}$ for all combinations of α and β in terms of two-centre integrals. The exact analytical form assumed for these integrals varies depending on the variant of the TB method. The NRL-TB method uses the following form:

$$H_\gamma(R) = \big(e_\gamma + f_\gamma R + g_\gamma R^2\big) \exp\big(-h_\gamma^2 R\big) F_c(R), \tag{7}$$

e_γ, f_γ, g_γ and h_γ being parameters.

The situation for the overlap matrix is similar. The on-site terms are, trivially, $S_{i\alpha,i\beta}=\delta_{\alpha\beta}$, while the form of the off-site elements is the same as for the Hamiltonian, except that the overlap two-center integrals have a slightly modified form:

$$S_\gamma(R)=\left(\delta_{qq'}+p_\gamma R+q_\gamma R^2+r_\gamma R^3\right)\exp\left(-s_\gamma^2 R\right)F_c(R), \tag{8}$$

p_γ, q_γ, r_γ and s_γ being parameters. $\delta_{qq'}$ assumes the value of 1 if the orbital types in γ are alike (*i.e.* $\gamma\in\{ss\sigma, pp\sigma, pp\pi, dd\sigma, dd\pi, dd\delta\}$) and 0 otherwise – this modification helps to keep the overlap matrix positive definite.

To calculate the force acting on any atom k in a TBMD simulation, Equation (2) is solved by direct diagonalization and the Hellmann-Feynman theorem [7] is employed, yielding:

$$\vec{F}_k=-\frac{\langle\Psi|\nabla_k(\hat{H}-\varepsilon\hat{S})|\Psi\rangle}{\langle\Psi|\Psi\rangle}=-2\left[\sum_n^{\mathrm{occ}}\sum_\alpha c_{k\alpha}^n\sum_{j\neq k}\sum_\beta c_{j\beta}^n\left(\frac{\partial\mathcal{H}_{k\alpha,j\beta}}{\partial\vec{R}_k}-\varepsilon_n\frac{\partial\mathcal{S}_{k\alpha,j\beta}}{\partial\vec{R}_k}\right)\right]. \tag{9}$$

The sums in Equation (9) run over all occuppied eigenstates n, all orbitals α of the atom k, all other atoms j and all their orbitals β, respectively. The factor of 2 is a consequence of spin degeneracy. In this non-self-consistent formulation, the derivatives of the basis set (Pulay contributions [8]) vanish identically [9, 10]. It is important to note that in the NRL-TB method the expression for the total energy lacks the otherwise typical repulsive potential part, due to clever shifting of eigenvalues in the underlying Kohn-Sham equation [1]. Thus, there is also no derivative of the repulsive potential present in the above expression for the ionic force.

In practical calculations the above expression is rearranged to take advantage of the fact that neither $\frac{\partial\mathcal{H}_{k\alpha,j\beta}}{\partial\vec{R}_k}$ nor $\frac{\partial\mathcal{S}_{k\alpha,j\beta}}{\partial\vec{R}_k}$ depend on n and these derivatives need to be calculated only once for each matrix element.

3. Calculation of the matrix element derivatives

Let us first consider the derivatives of the on-site terms of the Hamiltonian matrix. Applying the chain rule to Equation (3) yields an expression for the gradient:

$$\begin{aligned}\frac{\partial\mathcal{H}_{i\alpha,i\beta}}{\partial\vec{R}_k}&=\frac{\partial\mathcal{H}_{i\alpha,i\beta}}{\partial\varrho_i}\frac{\partial\varrho_i}{\partial\vec{R}_k}\\&=\frac{2}{3}\left(b_q\varrho_i^{-1/3}+2c_q\varrho_i^{1/3}+3d_q\varrho_i\right)\frac{\partial}{\partial\vec{R}_k}\left(\sum_{j\neq i}\exp(-\lambda^2R_{ij})F_c(R_{ij})\right).\end{aligned} \tag{10}$$

Two points should be noted here. First, only the neighbours of atom i that are closer than R_c need to be included in the above sum, since the cutoff function makes the other terms vanish. Second, only terms with $k=i$ or $k=j$ remain in the sum, since $\underset{\substack{k\neq i\\k\neq j}}{\forall}\frac{\partial R_{ij}}{\partial\vec{R}_k}=0$. Therefore, Equation (10) becomes

$$\begin{aligned}\frac{\partial\mathcal{H}_{i\alpha,i\beta}}{\partial\vec{R}_k}=\frac{2}{3}\left(b_q\varrho_i^{-1/3}+2c_q\varrho_i^{1/3}+3d_q\varrho_i\right)\times\sum_{\substack{j\neq i\\R_{ij}<R_c}}\Bigg[&(\delta_{ki}+\delta_{kj})\exp(-\lambda^2R_{ij})F_c(R_{ij})\\&\times\left(\ell^{-1}\exp\left(\frac{R_{ij}-R_c}{\ell}+5\right)F_c(R_{ij})+\lambda^2\right)\frac{\partial R_{ij}}{\partial\vec{R}_j}(-1)^{\delta_{kj}}\Bigg],\end{aligned} \tag{11}$$

where $\frac{\partial R_{ij}}{\partial \vec{R}_j} = [l, m, n]$ is the vector of direction cosines of the bond joining atoms i and j.

Let us now turn to the off-site elements of the Hamiltonian. Differentiating Equation (6), we first obtain:

$$\frac{\partial \mathcal{H}_{i\alpha,j\beta}}{\partial \vec{R}_k} = \sum_{s=1}^{3} \frac{\partial \Phi_{s,\alpha\beta}}{\partial \vec{R}_k} H_{\gamma_s}(R_{ij}) + \sum_{s=1}^{3} \Phi_{s,\alpha\beta} \frac{\partial H_{\gamma_s}(R_{ij})}{\partial \vec{R}_k}. \tag{12}$$

We note that the above derivative is non-zero only if $k = i$ or $k = j$. Let us consider the case where $k = i$ and denote the gradient represented by the first sum in the above equation by $\frac{1}{R_{ij}} \left[D^{(x)}_{\alpha,\beta}, D^{(y)}_{\alpha,\beta}, D^{(z)}_{\alpha,\beta} \right]$. The formulae for the components $D^{(x)}_{\alpha,\beta}$, $D^{(y)}_{\alpha,\beta}$*and* $D^{(z)}_{\alpha,\beta}$ are presented in the Appendix. For $k = j$ the negative of the respective formula should be taken.

Considering the second sum, we note that it is the same as Equation (6) (these are the formulae given in the original Slater-Koster paper [6]), save that the two-center integrals $H_\gamma(R_{ij})$ are replaced by their gradients with respect to $\vec{R}_k$. Each of these gradients can be computed as:

$$\begin{aligned} \frac{\partial H_\gamma(R_{ij})}{\partial \vec{R}_k} &= [l,m,n] \exp\left(-h_\gamma^2 R_{ij}\right) F_c(R_{ij}) \\ &\quad \times \left[\left(e_\gamma + f_\gamma R_{ij} + g_\gamma R_{ij}^2\right) \left(\ell^{-1} \exp\left(\frac{R_{ij} - R_c}{\ell} + 5 \right) F_c(R_{ij}) + h_\gamma^2 \right) \right. \\ &\quad \left. - \left(f_\gamma + 2 g_\gamma R_{ij}\right) \right], \end{aligned} \tag{13}$$

if $k = i$, the negative of the above if $k = j$, or zero otherwise.

Let us now focus on the derivatives of the overlap matrix elements. The derivatives of the on-site terms all vanish identically. The derivatives of the off-site terms behave in the same manner as those of the Hamiltonian matrix, but since the form of the overlap two-center integrals is slightly different (cf. Equation (8)), so is the form of their gradients, given by:

$$\begin{aligned} \frac{\partial H_\gamma(R_{ij})}{\partial \vec{R}_k} &= [l,m,n] \exp\left(-h_\gamma^2 R_{ij}\right) F_c(R_{ij}) \\ &\quad \times \left[\left(\delta_{qq'} + e_\gamma R_{ij} + f_\gamma R_{ij}^2 + g_\gamma R_{ij}^3\right) \left(\ell^{-1} \exp\left(\frac{R_{ij} - R_c}{\ell} + 5 \right) F_c(R_{ij}) + h_\gamma^2 \right) \right. \\ &\quad \left. - \left(e_\gamma + 2 f_\gamma R_{ij} + 3 g_\gamma R_{ij}^2\right) \right]. \end{aligned} \tag{14}$$

In practice, it is advantageous to store precalulated derivatives of all non-zero matrix elements, since they do not depend on eigenlevels, n, and are needed many times during the evaluation of the forces.

4. Conclusion

In this paper we have shown a prescription to calculate ionic forces in an MD simulation driven by the NRL-TB model. The forces have been obtained using the Hellmann-Feynman theorem and formulae for all matrix element derivatives have been

given. Derivatives of the on-site elements and the two-centre integrals, specific to the NRL-TB formulation, have been shown. Derivatives of the angular part of the off-site elements, characteristic of all TB formulations, have been included in the Appendix. We have assumed the system under study to be monoatomic: binary alloys and other systems containing more that one species remain beyond the scope of this paper.

The expressions presented have been incorporated into a TBMD program, *nanoTB* [11], capable of performing both cross-scaling TB+MD simulations (in which only a subset of the system is treated with the TB method) and non-cross-scaling TBMD simulations (in which forces on all atoms within the system are obtained from the TB method). Using this program, we have managed to reproduce the results of Kirchhoff *et al.* [4] for liquid gold, presented elsewhere [12]. The program has also been used with success to investigate the process of nanoindentation of copper (results presented in [13]). This validates the expressions given in this paper and attests to the usefulness of TB-driven molecular-dynamics.

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Appendix

This appendix contains explicit expressions for the x, y and z components of the gradient appearing in Equation (12) for all combinations of basis functions α and β. Notably, permuting indices α and β results in a sign change if and only if the sum of the parities of the orbitals is odd.

$$
\begin{aligned}
D^{(x)}_{s,s} &= 0\\
D^{(x)}_{s,x} &= (-1+l^2)H_{sp\sigma}\\
D^{(x)}_{s,y} &= lmH_{sp\sigma}\\
D^{(x)}_{s,z} &= lnH_{sp\sigma}\\
D^{(x)}_{s,xy} &= \sqrt{3}(-1+2l^2)mH_{sd\sigma}\\
D^{(x)}_{s,yz} &= 2\sqrt{3}lmnH_{sd\sigma}\\
D^{(x)}_{s,zx} &= \sqrt{3}(-1+2l^2)nH_{sd\sigma}\\
D^{(x)}_{s,x^2-y^2} &= \sqrt{3}l(-1+l^2-m^2)H_{sd\sigma}\\
D^{(x)}_{s,3z^2-r^2} &= -l(-1+l^2+m^2-2n^2)H_{sd\sigma}\\
D^{(x)}_{x,x} &= -2l(-1+l^2)(H_{pp\pi}-H_{pp\sigma})\\
D^{(x)}_{x,y} &= -(-1+2l^2)m(H_{pp\pi}-H_{pp\sigma})\\
D^{(x)}_{x,z} &= -(-1+2l^2)n(H_{pp\pi}-H_{pp\sigma})\\
D^{(x)}_{x,xy} &= lm((5-6l^2)H_{pd\pi}+\sqrt{3}(-2+3l^2)H_{pd\sigma})\\
D^{(x)}_{x,yz} &= -(-1+3l^2)mn(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(x)}_{x,zx} &= ln((5-6l^2)H_{pd\pi}+\sqrt{3}(-2+3l^2)H_{pd\sigma})\\
D^{(x)}_{x,x^2-y^2} &= \tfrac{1}{2}(-2(-1+3l^2)(-1+l^2-m^2)H_{pd\pi}+\sqrt{3}(3l^2l^2+m^2-3l^2(1+m^2))H_{pd\sigma})\\
D^{(x)}_{x,3z^2-r^2} &= \tfrac{1}{2}(-2\sqrt{3}(-1+3l^2)n^2H_{pd\pi}+(m^2-2n^2-3l^2(-1+l^2+m^2-2n^2))H_{pd\sigma})\\
D^{(x)}_{y,y} &= 2lm^2(-H_{pp\pi}+H_{pp\sigma})
\end{aligned}
$$

$$
\begin{aligned}
D^{(x)}_{y,z} &= 2lmn(-H_{pp\pi}+H_{pp\sigma})\\
D^{(x)}_{y,xy} &= (-1+2m^2+l^2(1-6m^2))H_{pd\pi}+\sqrt{3}(-1+3l^2)m^2H_{pd\sigma}\\
D^{(x)}_{y,yz} &= ln((1-6m^2)H_{pd\pi}+3\sqrt{3}m^2H_{pd\sigma})\\
D^{(x)}_{y,zx} &= -(-1+3l^2)mn(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(x)}_{y,x^2-y^2} &= \tfrac{1}{2}lm((2-6l^2+6m^2)H_{pd\pi}+\sqrt{3}(-2+3l^2-3m^2)H_{pd\sigma})\\
D^{(x)}_{y,3z^2-r^2} &= -\tfrac{1}{2}lm(6\sqrt{3}n^2H_{pd\pi}+(-2+3l^2+3m^2-6n^2)H_{pd\sigma})\\
D^{(x)}_{z,p_z} &= 2ln^2(-H_{pp\pi}+H_{pp\sigma})\\
D^{(x)}_{z,xy} &= -(-1+3l^2)mn(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(x)}_{z,yz} &= lm((1-6n^2)H_{pd\pi}+3\sqrt{3}n^2H_{pd\sigma})\\
D^{(x)}_{z,zx} &= (-1+2n^2+l^2(1-6n^2))H_{pd\pi}+\sqrt{3}(-1+3l^2)n^2H_{pd\sigma}\\
D^{(x)}_{z,x^2-y^2} &= -\tfrac{1}{2}l(-2+3l^2-3m^2)n(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(x)}_{z,3z^2-r^2} &= \tfrac{1}{2}(l(-2+3l^2+3m^2)n(2\sqrt{3}H_{pd\pi}-H_{pd\sigma})+6ln^2nH_{pd\sigma})\\
D^{(x)}_{xy,xy} &= 2l(((-1+2l^2)m^2+n^2)H_{dd\delta}+(-1+l^2+5m^2-8l^2m^2)H_{dd\pi}\\
&\quad +3(-1+2l^2)m^2H_{dd\sigma})\\
D^{(x)}_{xy,yz} &= n((1-m^2+l^2(-2+4m^2))H_{dd\delta}+(-1+4m^2+2l^2(1-8m^2))H_{dd\pi}\\
&\quad +3(-1+4l^2)m^2H_{dd\sigma})\\
D^{(x)}_{xy,zx} &= 2lmn(2(-1+l^2)H_{dd\delta}+(5-8l^2)H_{dd\pi}+3(-1+2l^2)H_{dd\sigma})\\
D^{(x)}_{xy,x^2-y^2} &= \tfrac{1}{2}m(4l^2l^2+m^2-l^2(3+4m^2))(H_{dd\delta}-4H_{dd\pi}+3H_{dd\sigma})\\
D^{(x)}_{xy,3z^2-r^2} &= -\tfrac{1}{2}\sqrt{3}m((1+n^2-2l^2(1+2n^2))H_{dd\delta}+4(-1+4l^2)n^2H_{dd\pi}\\
&\quad +(-m^2+2n^2+l^2(-3+4l^2+4m^2-8n^2))H_{dd\sigma})\\
D^{(x)}_{yz,yz} &= 2l((-1+l^2+2m^2n^2)H_{dd\delta}+(m^2+n^2-8m^2n^2)H_{dd\pi}+6m^2n^2H_{dd\sigma})\\
D^{(x)}_{yz,zx} &= m((1-n^2+l^2(-2+4n^2))H_{dd\delta}+(-1+4n^2+2l^2(1-8n^2))H_{dd\pi}\\
&\quad +3(-1+4l^2)n^2H_{dd\sigma})\\
D^{(x)}_{yz,x^2-y^2} &= lmn((1+2l^2-2m^2)H_{dd\delta}+2H_{dd\pi}-2(l-m)(l+m)(4H_{dd\pi}-3H_{dd\sigma})-3H_{dd\sigma})\\
D^{(x)}_{yz,3z^2-r^2} &= \sqrt{3}lmn((1-2l^2-2m^2)H_{dd\delta}+(-2+4l^2+4m^2-4n^2)H_{dd\pi}\\
&\quad -2(l^2+m^2-2n^2-\tfrac{1}{2})H_{dd\sigma})\\
D^{(x)}_{zx,zx} &= 2l((m^2+(-1+2l^2)n^2)H_{dd\delta}+(-1+l^2+5n^2-8l^2n^2)H_{dd\pi}+3(-1+2l^2)n^2H_{dd\sigma})\\
D^{(x)}_{zx,x^2-y^2} &= \tfrac{1}{2}n((2+4l^2l^2+m^2-l^2(7+4m^2))H_{dd\delta}-2(1+8l^2l^2+2m^2-8l^2(1+m^2))H_{dd\pi}\\
&\quad +3(4l^2l^2+m^2-l^2(3+4m^2))H_{dd\sigma})\\
D^{(x)}_{zx,3z^2-r^2} &= \tfrac{1}{2}\sqrt{3}n(-2(-1+4l^2)n^2(H_{dd\pi}-H_{dd\sigma})\\
&\quad -(4l^2l^2-m^2+l^2(-3+4m^2))(H_{dd\delta}-2H_{dd\pi}+H_{dd\sigma}))\\
D^{(x)}_{x^2-y^2,x^2-y^2} &= l((l^2l^2+m^2+m^2m^2-l^2(1+2m^2)+2n^2)H_{dd\delta}\\
&\quad -2(1+2l^2l^2+m^2+2m^2m^2-l^2(3+4m^2))H_{dd\pi}\\
&\quad +3(l-m)(l+m)(-1+l^2-m^2)H_{dd\sigma})\\
D^{(x)}_{x^2-y^2,3z^2-r^2} &= \tfrac{1}{2}\sqrt{3}l((-1+l^2-m^2+(-1+2l^2-2m^2)n^2)H_{dd\delta}-4(-1+2l^2-2m^2)n^2H_{dd\pi}\\
&\quad +2(l^2-l^2l^2+m^2m^2+(-1+2l^2-2m^2)n^2)H_{dd\sigma})\\
D^{(x)}_{3z^2-r^2,3z^2-r^2} &= l(-6n^2H_{dd\pi}+3(l^2+m^2)((-1+l^2+m^2)H_{dd\delta}+4n^2H_{dd\pi})\\
&\quad +(-1+l^2+m^2-2n^2)(l^2+m^2-2n^2)H_{dd\sigma})\\
D^{(y)}_{s,s} &= 0\\
D^{(y)}_{s,x} &= lmH_{sp\sigma}\\
D^{(y)}_{s,y} &= (-1+m^2)H_{sp\sigma}
\end{aligned}
$$

$$
\begin{aligned}
D^{(y)}_{s,z} &= mn\,H_{sp\sigma}\\
D^{(y)}_{s,xy} &= \sqrt{3}l(-1+2m^2)\,H_{sd\sigma}\\
D^{(y)}_{s,yz} &= \sqrt{3}(-1+2m^2)n\,H_{sd\sigma}\\
D^{(y)}_{s,zx} &= 2\sqrt{3}lmn\,H_{sd\sigma}\\
D^{(y)}_{s,x^2-y^2} &= -\sqrt{3}m(-1-l^2+m^2)\,H_{sd\sigma}\\
D^{(y)}_{s,3z^2-r^2} &= -m(-1+l^2+m^2-2n^2)\,H_{sd\sigma}\\
D^{(y)}_{x,x} &= 2l^2m(-H_{pp\pi}+H_{pp\sigma})\\
D^{(y)}_{x,y} &= -l(-1+2m^2)(H_{pp\pi}-H_{pp\sigma})\\
D^{(y)}_{x,z} &= 2lmn(-H_{pp\pi}+H_{pp\sigma})\\
D^{(y)}_{x,xy} &= (-1+m^2+l^2(2-6m^2))\,H_{pd\pi}+\sqrt{3}l^2(-1+3m^2)\,H_{pd\sigma}\\
D^{(y)}_{x,yz} &= -l(-1+3m^2)n(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(y)}_{x,zx} &= mn((1-6l^2)\,H_{pd\pi}+3\sqrt{3}l^2\,H_{pd\sigma})\\
D^{(y)}_{x,x^2-y^2} &= \tfrac{1}{2}lm((-2-6l^2+6m^2)\,H_{pd\pi}+\sqrt{3}(2+3l^2-3m^2)\,H_{pd\sigma})\\
D^{(y)}_{x,3z^2-r^2} &= -\tfrac{1}{2}lm(6\sqrt{3}n^2\,H_{pd\pi}+(-2+3l^2+3m^2-6n^2)\,H_{pd\sigma})\\
D^{(y)}_{y,y} &= -2m(-1+m^2)(H_{pp\pi}-H_{pp\sigma})\\
D^{(y)}_{y,z} &= -(-1+2m^2)n(H_{pp\pi}-H_{pp\sigma})\\
D^{(y)}_{y,xy} &= lm((5-6m^2)\,H_{pd\pi}+\sqrt{3}(-2+3m^2)\,H_{pd\sigma})\\
D^{(y)}_{y,yz} &= mn((5-6m^2)\,H_{pd\pi}+\sqrt{3}(-2+3m^2)\,H_{pd\sigma})\\
D^{(y)}_{y,zx} &= -l(-1+3m^2)n(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(y)}_{y,x^2-y^2} &= \tfrac{1}{2}(-2(1+l^2-m^2)(-1+3m^2)\,H_{pd\pi}+\sqrt{3}(-l^2+3(1+l^2)m^2-3m^2m^2)\,H_{pd\sigma})\\
D^{(y)}_{y,3z^2-r^2} &= \tfrac{1}{2}(-2(-1+3m^2)n^2(\sqrt{3}H_{pd\pi}-H_{pd\sigma})+l^2\,H_{pd\sigma}-3m^2(-1+l^2+m^2)\,H_{pd\sigma})\\
D^{(y)}_{z,z} &= 2mn^2(-H_{pp\pi}+H_{pp\sigma})\\
D^{(y)}_{z,xy} &= -l(-1+3m^2)n(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(y)}_{z,yz} &= (-1+2n^2+m^2(1-6n^2))\,H_{pd\pi}+\sqrt{3}(-1+3m^2)n^2\,H_{pd\sigma}\\
D^{(y)}_{z,zx} &= lm((1-6n^2)\,H_{pd\pi}+3\sqrt{3}n^2\,H_{pd\sigma})\\
D^{(y)}_{z,x^2-y^2} &= \tfrac{1}{2}m(-2-3l^2+3m^2)n(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(y)}_{z,3z^2-r^2} &= \tfrac{1}{2}(m(-2+3l^2+3m^2)n(2\sqrt{3}H_{pd\pi}-H_{pd\sigma})+6mn^2n\,H_{pd\sigma})\\
D^{(y)}_{xy,xy} &= 2m((l^2(-1+2m^2)+n^2)\,H_{dd\delta}+(-1+m^2+l^2(5-8m^2))\,H_{dd\pi}\\
&\quad +3l^2(-1+2m^2)\,H_{dd\sigma})\\
D^{(y)}_{xy,yz} &= 2lmn(2(-1+m^2)\,H_{dd\delta}+(5-8m^2)\,H_{dd\pi}+3(-1+2m^2)\,H_{dd\sigma})\\
D^{(y)}_{xy,zx} &= n((1-2m^2+l^2(-1+4m^2))\,H_{dd\delta}+(-1+2m^2+4l^2(1-4m^2))\,H_{dd\pi}\\
&\quad +3l^2(-1+4m^2)\,H_{dd\sigma})\\
D^{(y)}_{xy,x^2-y^2} &= \tfrac{1}{2}l(3m^2-4m^2m^2+l^2(-1+4m^2))(H_{dd\delta}-4H_{dd\pi}+3H_{dd\sigma})\\
D^{(y)}_{xy,3z^2-r^2} &= -\tfrac{1}{2}\sqrt{3}l((1+n^2-2m^2(1+2n^2))\,H_{dd\delta}+4(-1+4m^2)n^2\,H_{dd\pi}\\
&\quad +(l^2(-1+4m^2)+2n^2+m^2(-3+4m^2-8n^2))\,H_{dd\sigma})\\
D^{(y)}_{yz,yz} &= 2m((l^2+(-1+2m^2)n^2)\,H_{dd\delta}+(-1+m^2+5n^2-8m^2n^2)\,H_{dd\pi}\\
&\quad +3(-1+2m^2)n^2\,H_{dd\sigma})\\
D^{(y)}_{yz,zx} &= l((1-n^2+m^2(-2+4n^2))\,H_{dd\delta}+(-1+4n^2+2m^2(1-8n^2))\,H_{dd\pi}\\
&\quad +3(-1+4m^2)n^2\,H_{dd\sigma})\\
D^{(y)}_{yz,x^2-y^2} &= \tfrac{1}{2}n((-2+7m^2-4m^2m^2+l^2(-1+4m^2))\,H_{dd\delta}\\
&\quad +2(1+2l^2-8(1+l^2)m^2+8m^2m^2)\,H_{dd\pi}+3(3m^2-4m^2m^2+l^2(-1+4m^2))\,H_{dd\sigma})
\end{aligned}
$$

$$
\begin{aligned}
D^{(y)}_{yz,3z^2-r^2} &= \sqrt{3}\,\tfrac{1}{2}\,n(-2(-1+4m^2)n^2(H_{dd\pi}-H_{dd\sigma})\\
&\quad -(-l^2+(-3+4l^2)m^2+4m^2m^2)(H_{dd\delta}-2H_{dd\pi}+H_{dd\sigma}))\\
D^{(y)}_{zx,zx} &= 2m((-1+m^2+2l^2n^2)H_{dd\delta}+(l^2+n^2-8l^2n^2)H_{dd\pi}+6l^2n^2H_{dd\sigma})\\
D^{(y)}_{zx,x^2-y^2} &= lmn((-1+2l^2-2m^2)H_{dd\delta}-2H_{dd\pi}-2(l-m)(l+m)(4H_{dd\pi}-3H_{dd\sigma})+3H_{dd\sigma})\\
D^{(y)}_{zx,3z^2-r^2} &= \sqrt{3}lmn((1-2l^2-2m^2)H_{dd\delta}+(-2+4l^2+4m^2-4n^2)H_{dd\pi}+H_{dd\sigma}\\
&\quad -2(l^2+m^2-2n^2)H_{dd\sigma})\\
D^{(y)}_{x^2-y^2,x^2-y^2} &= m((l^2l^2-m^2+m^2m^2+l^2(1-2m^2)+2n^2)H_{dd\delta}\\
&\quad -2(1+l^2+2l^2l^2-(3+4l^2)m^2+2m^2m^2)H_{dd\pi}+3(l-m)(l+m)(1+l^2-m^2)H_{dd\sigma})\\
D^{(y)}_{x^2-y^2,3z^2-r^2} &= \tfrac{1}{2}\sqrt{3}m((1+l^2-m^2+(1+2l^2-2m^2)n^2)H_{dd\delta}-4(1+2l^2-2m^2)n^2H_{dd\pi}\\
&\quad +2(-l^2l^2-m^2+m^2m^2+(1+2l^2-2m^2)n^2)H_{dd\sigma})\\
D^{(y)}_{3z^2-r^2,3z^2-r^2} &= m(-6n^2H_{dd\pi}+3(l^2+m^2)((-1+l^2+m^2)H_{dd\delta}+4n^2H_{dd\pi})\\
&\quad +(-1+l^2+m^2-2n^2)(l^2+m^2-2n^2)H_{dd\sigma})\\
D^{(z)}_{s,s} &= 0\\
D^{(z)}_{s,x} &= lnH_{sp\sigma}\\
D^{(z)}_{s,y} &= mnH_{sp\sigma}\\
D^{(z)}_{s,z} &= (-1+n^2)H_{sp\sigma}\\
D^{(z)}_{s,xy} &= 2\sqrt{3}lmnH_{sd\sigma}\\
D^{(z)}_{s,yz} &= \sqrt{3}m(-1+2n^2)H_{sd\sigma}\\
D^{(z)}_{s,zx} &= \sqrt{3}l(-1+2n^2)H_{sd\sigma}\\
D^{(z)}_{s,x^2-y^2} &= \sqrt{3}(l-m)(l+m)nH_{sd\sigma}\\
D^{(z)}_{s,3z^2-r^2} &= n(-2-l^2-m^2+2n^2)H_{sd\sigma}\\
D^{(z)}_{x,x} &= 2l^2n(-H_{pp\pi}+H_{pp\sigma})\\
D^{(z)}_{x,y} &= 2lmn(-H_{pp\pi}+H_{pp\sigma})\\
D^{(z)}_{x,z} &= -l(-1+2n^2)(H_{pp\pi}-H_{pp\sigma})\\
D^{(z)}_{x,xy} &= mn((1-6l^2)H_{pd\pi}+3\sqrt{3}l^2H_{pd\sigma})\\
D^{(z)}_{x,yz} &= -lm(-1+3n^2)(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(z)}_{x,zx} &= (-1+n^2+l^2(2-6n^2))H_{pd\pi}+\sqrt{3}l^2(-1+3n^2)H_{pd\sigma}\\
D^{(z)}_{x,x^2-y^2} &= \tfrac{1}{2}ln((2-6l^2+6m^2)H_{pd\pi}+3\sqrt{3}(l-m)(l+m)H_{pd\sigma})\\
D^{(z)}_{x,3z^2-r^2} &= -\tfrac{1}{2}ln(2\sqrt{3}(-2+3n^2)H_{pd\pi}+(4+3l^2+3m^2-6n^2)H_{pd\sigma})\\
D^{(z)}_{y,y} &= 2m^2n(-H_{pp\pi}+H_{pp\sigma})\\
D^{(z)}_{y,z} &= -m(-1+2n^2)(H_{pp\pi}-H_{pp\sigma})\\
D^{(z)}_{y,xy} &= ln((1-6m^2)H_{pd\pi}+3\sqrt{3}m^2H_{pd\sigma})\\
D^{(z)}_{y,yz} &= (-1+n^2+m^2(2-6n^2))H_{pd\pi}+\sqrt{3}m^2(-1+3n^2)H_{pd\sigma}\\
D^{(z)}_{y,zx} &= -lm(-1+3n^2)(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(z)}_{y,x^2-y^2} &= \tfrac{1}{2}mn((-2-6l^2+6m^2)H_{pd\pi}+3\sqrt{3}(l-m)(l+m)H_{pd\sigma})\\
D^{(z)}_{y,3z^2-r^2} &= -\tfrac{1}{2}mn(2\sqrt{3}(-2+3n^2)H_{pd\pi}+(4+3l^2+3m^2-6n^2)H_{pd\sigma})\\
D^{(z)}_{z,z} &= -2n(-1+n^2)(H_{pp\pi}-H_{pp\sigma})\\
D^{(z)}_{z,xy} &= -lm(-1+3n^2)(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})\\
D^{(z)}_{z,yz} &= mn((5-6n^2)H_{pd\pi}+\sqrt{3}(-2+3n^2)H_{pd\sigma})\\
D^{(z)}_{z,zx} &= ln((5-6n^2)H_{pd\pi}+\sqrt{3}(-2+3n^2)H_{pd\sigma})\\
D^{(z)}_{z,x^2-y^2} &= -\tfrac{1}{2}(l-m)(l+m)(-1+3n^2)(2H_{pd\pi}-\sqrt{3}H_{pd\sigma})
\end{aligned}
$$

$$
\begin{aligned}
D^{(z)}_{z,3z^2-r^2} &= \tfrac{1}{2}\,(2\sqrt{3}(l^2+m^2)(-1+3n^2)\,H_{pd\pi}+(l^2+m^2-3(2+l^2+m^2)n^2+6n^2n^2)\,H_{pd\sigma})\\
D^{(z)}_{xy,xy} &= 2n\,((-1+2l^2m^2+n^2)\,H_{dd\delta}+(l^2+m^2-8l^2m^2)\,H_{dd\pi}+6l^2m^2\,H_{dd\sigma})\\
D^{(z)}_{xy,yz} &= l\,((1-2n^2+m^2(-1+4n^2))\,H_{dd\delta}+(-1+2n^2+4m^2(1-4n^2))\,H_{dd\pi}\\
&\quad +3m^2(-1+4n^2)\,H_{dd\sigma})\\
D^{(z)}_{xy,zx} &= m\,((1-2n^2+l^2(-1+4n^2))\,H_{dd\delta}+(-1+2n^2+4l^2(1-4n^2))\,H_{dd\pi}\\
&\quad +3l^2(-1+4n^2)\,H_{dd\sigma})\\
D^{(z)}_{xy,x^2-y^2} &= 2l\,(l-m)\,m\,(l+m)\,n\,(H_{dd\delta}-4H_{dd\pi}+3H_{dd\sigma})\\
D^{(z)}_{xy,3z^2-r^2} &= -2\sqrt{3}\,l\,m\,n\,(-n^2\,H_{dd\delta}+(-2+4n^2)\,H_{dd\pi}+(1+l^2+m^2-2n^2)\,H_{dd\sigma})\\
D^{(z)}_{yz,yz} &= 2n\,((l^2+m^2(-1+2n^2))\,H_{dd\delta}+(-1+n^2+m^2(5-8n^2))\,H_{dd\pi}\\
&\quad +3m^2(-1+2n^2)\,H_{dd\sigma})\\
D^{(z)}_{yz,zx} &= 2l\,m\,n\,(2(-1+n^2)\,H_{dd\delta}+(5-8n^2)\,H_{dd\pi}+3(-1+2n^2)\,H_{dd\sigma})\\
D^{(z)}_{yz,x^2-y^2} &= \tfrac{1}{2}\,m\,((-2-l^2+m^2+4(1+l^2-m^2)n^2)\,H_{dd\delta}\\
&\quad -2(-1-2l^2+2m^2+2(1+4l^2-4m^2)n^2)\,H_{dd\pi}\\
&\quad +3(l-m)(l+m)(-1+4n^2)\,H_{dd\sigma})\\
D^{(z)}_{yz,3z^2-r^2} &= \tfrac{1}{2}\,\sqrt{3}\,m\,(-(l^2+m^2)(-1+4n^2)\,H_{dd\delta}\\
&\quad +(-2(l^2+m^2)+2(3+4l^2+4m^2)n^2-8n^2n^2)\,H_{dd\pi}\\
&\quad +(l^2+m^2-2(3+2l^2+2m^2)n^2+8n^2n^2)\,H_{dd\sigma})\\
D^{(z)}_{zx,zx} &= 2n\,((m^2+l^2(-1+2n^2))\,H_{dd\delta}+(-1+n^2+l^2(5-8n^2))\,H_{dd\pi}+3l^2(-1+2n^2)\,H_{dd\sigma})\\
D^{(z)}_{zx,x^2-y^2} &= \tfrac{1}{2}\,l\,((2+m^2-4(1+m^2)n^2+l^2(-1+4n^2))\,H_{dd\delta}\\
&\quad -2(1-2l^2+2m^2+2(-1+4l^2-4m^2)n^2)\,H_{dd\pi}+3(l-m)(l+m)(-1+4n^2)\,H_{dd\sigma})\\
D^{(z)}_{zx,3z^2-r^2} &= \tfrac{1}{2}\,\sqrt{3}\,l\,(-(l^2+m^2)(-1+4n^2)\,H_{dd\delta}\\
&\quad +(-2(l^2+m^2)+2(3+4l^2+4m^2)n^2-8n^2n^2)\,H_{dd\pi}\\
&\quad +(l^2+m^2-2(3+2l^2+2m^2)n^2+8n^2n^2)\,H_{dd\sigma})\\
D^{(z)}_{x^2-y^2,x^2-y^2} &= n\,((-2+l^2l^2-2l^2m^2+m^2m^2+2n^2)\,H_{dd\delta}\\
&\quad +2(l^2-2l^2l^2+m^2+4l^2m^2-2m^2m^2)\,H_{dd\pi}\\
&\quad +3(l^2-m^2)(l^2-m^2)\,H_{dd\sigma})\\
D^{(z)}_{x^2-y^2,3z^2-r^2} &= -\sqrt{3}\,(l-m)\,(l+m)\,n\,(-n^2\,H_{dd\delta}+(-2+4n^2)\,H_{dd\pi}+(1+l^2+m^2-2n^2)\,H_{dd\sigma})\\
D^{(z)}_{3z^2-r^2,3z^2-r^2} &= n\,(3(l^2+m^2)(l^2+m^2)\,H_{dd\delta}+6(l^2+m^2)(-1+2n^2)\,H_{dd\pi}\\
&\quad +(l^2+m^2-2n^2)(2+l^2+m^2-2n^2)\,H_{dd\sigma})
\end{aligned}
$$

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