IMPROVED FORCES FOR THE EXCHANGE-HOLE DIPOLE MOMENT MODEL

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INTRODUCTION AND MOTIVATION

London dispersion is a weak, attractive, intermolecular force that determines adhesion, friction, crystal structure packing, and the properties of layered materials. Most commonly-used DFT functionals do not account for dispersion, so a correction such as the exchange-hole dipole moment (XDM) model must be added. XDM has been successfully implemented in numerous electronic-structure codes, most recently FHI-aims and, when paired with hybrid functionals, has demonstrated unprecedented accuracy for molecular crystals. However, the current implementations of forces within most dispersion corrections, including XDM, erroneously assume that the dispersion coefficients are constant with respect to changing atomic positions and lattice vectors. While this assumption holds well for molecular crystals, it fails to accurately describe inorganic solids, such as bulk metals. This can introduce energy errors when performing geometry optimizations compared to manual scans of geometry and can also cause a cascading force error in molecular dynamics simulations. To address these issues, we are currently developing an improved version of XDM.

STRESS ERRORS IN GEOMETRY OPTIMIZATIONS

Here, we compare the lattice constant (a_{latt} in Å) and corresponding energy errors (ΔE in meV) for selected materials with cubic unit cells, computed in FHI-aims with the PBE functional and lightdense basis settings. a_{latt}^{min} is the interpolated minimum-energy lattice constant obtained via manually scanning the geometry, and a_{latt}^{rel} is the lattice constant obtained by a variable-cell relaxation. We see that XDM is disproportionately affected by the constant-C_6 assumption in its dispersion force calculation compared to the TS and MBD-NL methods.

	TS			MBD-NL			XDM		
	a_{latt}^{min}	a_{latt}^{rel}	ΔE	a_{latt}^{min}	a_{latt}^{rel}	ΔE	a_{latt}^{min}	a_{latt}^{rel}	ΔE
CO_2	5.92	5.93	01	5.92	5.93	<1	5.93	5.93	<1
Diam.	3.55	3.56	<1	3.56	3.56	<1	3.57	3.56	01
Si	5.47	5.46	<1	5.47	5.44	08	5.47	5.44	13
GaAs	5.73	5.73	<1	5.71	5.69	03	5.72	5.67	23
Ni	3.41	3.41	<1	3.47	3.47	<1	3.48	3.45	17
Cu	3.55	3.54	<1	3.60	3.60	<1	3.60	3.56	25
NaCl	5.38	5.40	02	5.62	5.63	<1	5.56	5.51	13
MgO	4.20	4.20	<1	4.26	4.24	02	4.24	4.22	15

These issues are not code-dependent. In the right column, we show results for NaCl (left) and CO_2 (right) when simulated with Quantum ESPRESSO using B86bPBE-XDM/PAW. Top: The PES showing the energy as a function of lattice constant and the result of a constant-C_n variable-cell relaxation. Middle: A comparison of the exact stress and that computed assuming constant dispersion coefficients. Bottom: The variation in the homoatomic C_6 dispersion coefficients relative to their equilibrium values.

BREAKDOWN OF THE CONSTANT C_6 ASSUMPTION
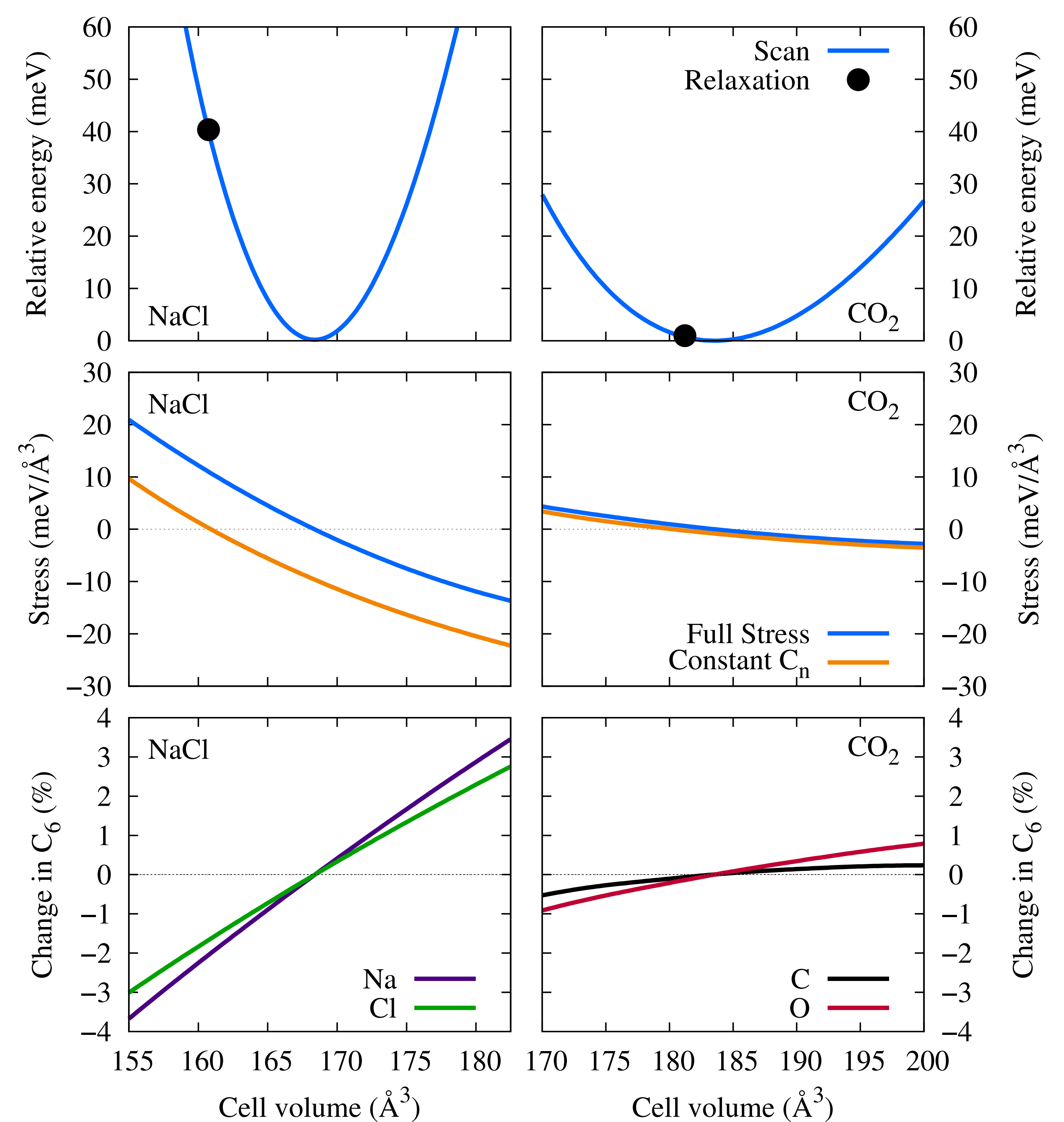
IMPROVED XDM FORCES IMPLEMENTATION

The XDM dispersion force, $\boldsymbol{F}^{XDM}$, depends on the derivative with respect to atomic positions. Via the chain rule, this can be written with respect to changing atomic distances between two atoms i and j, R_{ij}. Assuming non-constant dispersion coefficients, the improved XDM force expression for atom i is

$$\boldsymbol{F}_i^{XDM} = \sum_{\boldsymbol{L}} \sum_{j'} \sum_{n=6,8,10} \left[-n f_n^{BJ} \frac{C_{n,ij}^{XDM}}{R_{ij,\boldsymbol{L}}^{n+1}} + (f_n^{BJ})' \frac{C_{n,ij}^{XDM}}{R_{ij,\boldsymbol{L}}^n} + f_n^{BJ} \frac{(C_{n,ij}^{XDM})'}{R_{ij,\boldsymbol{L}}^n} \right] \hat{R}_{ij,\boldsymbol{L}} \,,$$

where j' indicates omitting the $j = i$ term for lattice vector $\boldsymbol{L} = 0$. The derivative of the Becke-Johnson damping function can easily be modified to reflect non-constant dispersion coefficients in the derivative of the van der Waals radius. The derivatives of the C_n dispersion coefficients (e.g. C_6),

$$\left(C_{6,ij}^{XDM} \right)' = \frac{\alpha_i^2 \langle M_1^2 \rangle_j^2 \left[\alpha_j \langle M_1^2 \rangle_i' + \alpha_j' \langle M_1^2 \rangle_i \right] + \alpha_j^2 \langle M_1^2 \rangle_i^2 \left[\alpha_i \langle M_1^2 \rangle_j' + \alpha_i' \langle M_1^2 \rangle_j \right]}{\left(\alpha_j \langle M_1^2 \rangle_i + \alpha_i \langle M_1^2 \rangle_j \right)^2} \,,$$

are written in terms of the derivatives of both the polarizability, α, and the multipole moment integrals,

$$\langle M_\ell^2 \rangle_i = \sum_\sigma \int \omega_i \, \rho_\sigma(\boldsymbol{r}) \left[r^\ell - (r - d_{X\sigma})^\ell \right]^2 d\boldsymbol{r} \,.$$

Here, ρ_σ is the electron density and $d_{X\sigma}$ is the exchange-hole dipole moment for spin state σ. To capture the derivatives of the above quantities with respect to atomic distance, we only need the derivative of the Hirshfeld weights, ω_i, which was recently implemented within the FHI-aims code.

FURTHER READING

- Implementation of XDM in FHI-aims: *Price, A. J. A., Otero-de-la-Roza, A. & Johnson, E. R., Chem. Sci.* **14**, 1252–1262 (2023)
- MBD-NL: *Hermann, J., & Tkatchenko, A., Phys. Rev. Lett.* **124**, 146401 (2020)
- Forces Issue Caused by Constant C_6: *Price, A. J. A., Bryenton, K. R., & Johnson, E. R., J. Chem. Phys.* **154**, 230902, (2021)
- Derivatives of the Hirshfeld Weights: *Heßelmann, A., J. Chem. Phys.* **149**, 044103, (2018)

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