

HOW ARE FORCES CALCULATED IN DENSITY-FUNCTIONAL THEORY?

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CHEM 6353: Density-Functional Theory

Forces in Density-Functional Theory

What Are Force Calculations?

Geometry Optimizations

Hellmann-Feynman Theorem: Derivation

Proof of the Hellmann-Feynman Theorem

Applying Hellmann-Feynman Theorem to DFT

Hellmann-Feynman Theorem: Examples

Expectation Value of $1/r$ for Hydrogen

Molecular Forces

Long-Range Interaction Forces for Separated Hydrogen

Implementation in Quantum ESPRESSO

The Geometry Optimization Loop

Relevant Code

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Forces in DFT

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QE Implementation

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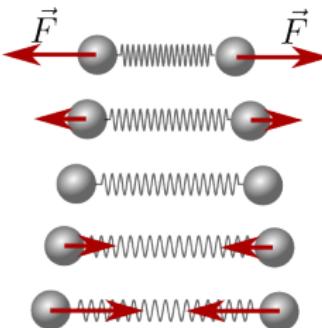
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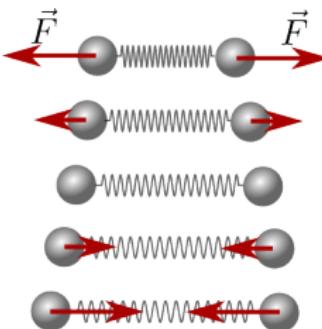
WHAT ARE FORCE CALCULATIONS?

- Electronic-structure theory software has a process called a geometry optimization.
- The forces on each atom are calculated in each geometry optimization step.
- The atom positions will be adjusted in the direction of the largest gradient.
- Once the atoms are moving sufficiently small within each step, they are said to be relaxed and the geometry is optimized.
- The system will adjust itself until it settles into a minimum in the potential energy surface.



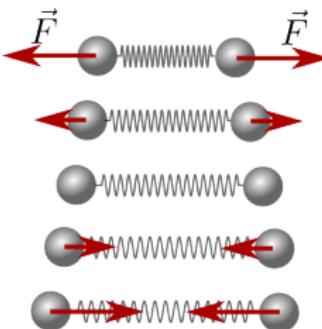
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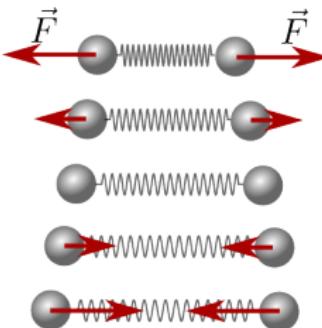
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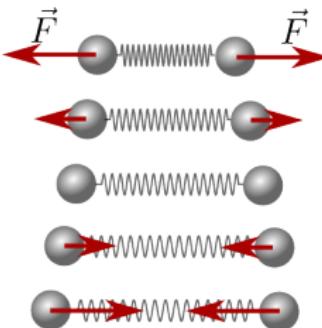
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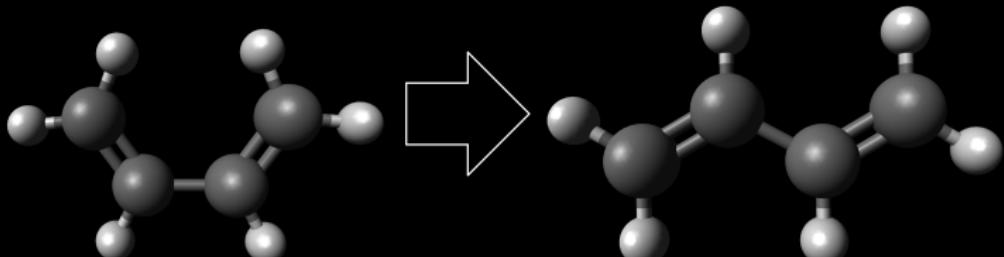
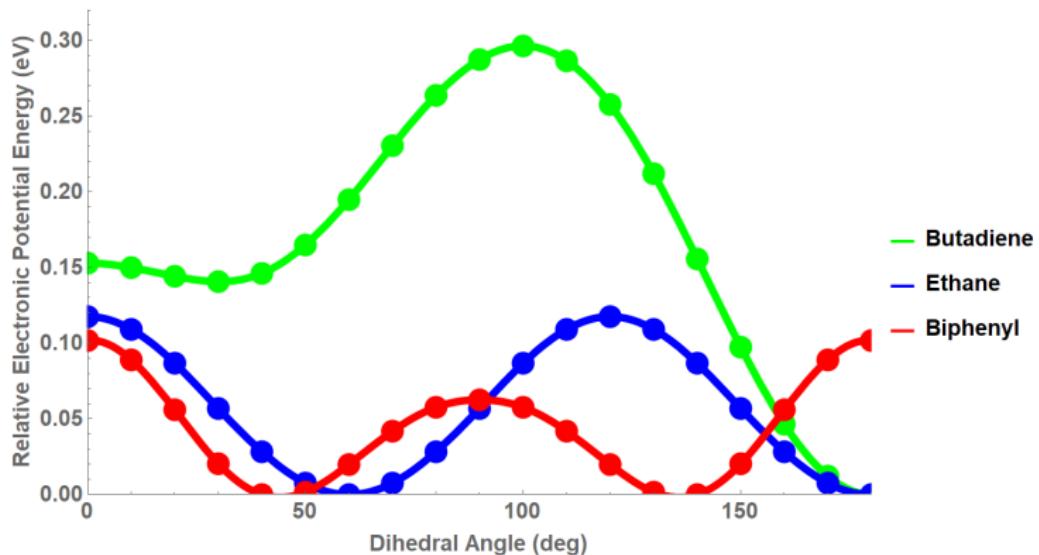


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POTENTIAL ENERGY SURFACES



GEOMETRY OPTIMIZATION OF CIS-OMETHOXYPHENOL

Relaxed Energy: 107.203 kJ/mol

Forces in DFT

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Hellmann-Feynman Theorem: Derivation

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Hellmann-Feynman Theorem: Examples

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QE Implementation

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GEOMETRY OPTIMIZATION OF TRANS-OMETHOXYPHENOL

Relaxed Energy: 67.7598 kJ/mol

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PROOF OF THE HELLMANN-FEYNMAN THEOREM

THE TIME-INDEPENDENT SCHRÖDINGER EQUATION:

$$\hat{H} |\psi(\mathbf{r})\rangle = E |\psi(\mathbf{r})\rangle$$

THE HELLMANN-FEYNMAN THEOREM:

$$\left\langle \psi(\mathbf{r}) \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi(\mathbf{r}) \right\rangle = \left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle = \frac{\partial E}{\partial \lambda}$$

where \hat{H} , $\psi(\mathbf{r})$ and E_n all depend on the continuous parameter λ .

PROOF

From the Schrödinger Equation, we have

$$\begin{aligned}\hat{H} |\psi\rangle &= E |\psi\rangle \\ \Rightarrow \langle\psi | \hat{H} | \psi\rangle &= \langle\psi | E | \psi\rangle \\ &= E \langle\psi | \psi\rangle \\ &= E . \quad \langle\psi | \psi\rangle = 1\end{aligned}$$

Then, assuming our terms are functions of some continuously varying parameter λ , we take the derivative of both sides

$$\frac{\partial}{\partial \lambda} \langle\psi | \hat{H} | \psi\rangle = \frac{\partial E}{\partial \lambda} .$$

The LHS may be expanded using product rule.

Thus,

$$\left\langle \frac{\partial \psi}{\partial \lambda} \left| \hat{H} \right| \psi \right\rangle + \left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle + \left\langle \psi \left| \hat{H} \right| \frac{\partial \psi}{\partial \lambda} \right\rangle = \frac{\partial E}{\partial \lambda}, \quad \text{via Product Rule}$$

$$E \left\langle \frac{\partial \psi}{\partial \lambda} \left| \psi \right\rangle + \left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle + E \left\langle \psi \left| \frac{\partial \psi}{\partial \lambda} \right\rangle = \frac{\partial E}{\partial \lambda}, \quad \hat{H} |\psi\rangle = E |\psi\rangle$$

$$E \frac{\partial}{\partial \lambda} \langle \psi | \psi \rangle + \left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle = \frac{\partial E}{\partial \lambda}, \quad \text{via Product Rule}$$

$$\left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle = \frac{\partial E}{\partial \lambda}, \quad \langle \psi | \psi \rangle = 1$$

and finally,

$$\left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle = \frac{\partial E}{\partial \lambda}.$$

□

APPLYING HELLMANN-FEYNMAN THEOREM TO DFT

THE HELLMANN-FEYNMAN THEOREM:

$$\left\langle \psi(\mathbf{r}) \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi(\mathbf{r}) \right\rangle = \left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle = \frac{\partial E}{\partial \lambda}$$

where \hat{H} , $\psi(\mathbf{r})$ and E_n all depend on the continuous parameter λ .

SPECIAL CASE:

HELLMANN-FEYNMAN THEOREM FOR FORCES:

$$\mathbf{F}_r = - \left\langle \frac{\partial \hat{H}}{\partial \mathbf{r}} \right\rangle = - \frac{\partial E}{\partial \mathbf{r}}$$

For conservative systems, the force can be expressed as the negative of the gradient of the potential energy,

$$\mathbf{F}(\mathbf{r}) = -\nabla V(\mathbf{r}).$$

As a basic example, we know that gravitational force is conservative, and gravitational potential energy is given by

$$U_g = mgz,$$

so the gravitational force may be expressed as

$$\begin{aligned}\mathbf{F} &= -\nabla U_g \\ &= -\frac{d}{dz} mgz \hat{\mathbf{z}} \\ &= -mg \hat{\mathbf{z}}.\end{aligned}$$

If we can show the forces at play in molecular systems are conservative, then we can use the Hellmann-Feynman theorem to calculate them via

$$\mathbf{F}_r = - \left\langle \frac{\partial \hat{H}}{\partial \mathbf{r}} \right\rangle = - \frac{\partial E}{\partial \mathbf{r}}.$$

When you take the derivative of the Hamiltonian with respect to some nuclear coordinate, the only surviving terms are the nuclear-electron and nuclear-nuclear terms.

These terms arise from electrostatics, so we only need to prove that the electrostatic force is conservative for our condition to be satisfied.

Without loss of generality, consider an attractive potential for the interaction between a nuclei and an electron. This force is described by

$$\mathbf{F}(\mathbf{r}) = \frac{e^2 Z}{4\pi\epsilon_0} \frac{1}{r^2} \hat{\mathbf{r}}.$$

There are a few ways to show a force is conservative. One way is to show the curl of the force is zero:

$$\nabla \times \mathbf{F}(\mathbf{r}) = 0.$$

Another way is to show that a force is conservative is to show that the work done along a path that starts and ends at the same point is zero, i.e.,

$$\oint_{\ell} \mathbf{F}(\mathbf{r}) \cdot d\ell = 0,$$

where the path is given by the differential displacement in spherical coordinates

$$d\ell = dr \hat{\mathbf{r}} + r d\theta \hat{\mathbf{\theta}} + r \sin(\theta) d\phi \hat{\mathbf{\phi}}.$$

Thus,

$$\begin{aligned}\oint_{\ell} \mathbf{F}(\mathbf{r}) \cdot d\ell &= \oint_{\ell} \left(\frac{e^2 Z}{4\pi\epsilon_0} \frac{1}{r^2} \hat{r} \right) \cdot (dr \hat{r} + rd\theta \hat{\theta} + r \sin(\theta) d\phi \hat{\phi}) \\&= \frac{e^2 Z}{4\pi\epsilon_0} \int_a^a \frac{1}{r^2} dr \\&= \frac{e^2 Z}{4\pi\epsilon_0} (-2) \left[\frac{1}{r^3} \right]_a^a \\&= \frac{-e^2 Z}{2\pi\epsilon_0} \left[\frac{1}{a^3} - \frac{1}{a^3} \right] \\&= 0.\end{aligned}$$

So the coulombic force is conservative, and the Hellmann-Feynman theorem may be used to obtain our molecular forces via

$$\mathbf{F}_r = - \left\langle \frac{\partial \hat{H}}{\partial \mathbf{r}} \right\rangle = - \frac{\partial E}{\partial \mathbf{r}}.$$

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EXPECTATION VALUE OF $1/r$ FOR HYDROGEN

The Hamiltonian and Energy for hydrogen is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2},$$
$$E_n = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2}.$$

From the Hellmann-Feynman theorem

$$\left\langle \frac{\partial \hat{H}}{\partial \lambda} \right\rangle = \frac{\partial E}{\partial \lambda},$$

we take $\lambda = e$, then

$$\left\langle \frac{\partial \hat{H}}{\partial e} \right\rangle = \frac{\partial E_n}{\partial e}.$$

C. Sánchez del Rio, *Evaluation of some averages for the hydrogen atom*, Am. J. Phys. **50**, 556 (1982)

D. Griffiths, *Introduction to Quantum Mechanics* 2ed, Pearson. p288 (2005)

Substituting in our values for \hat{H} and E_n yields

$$\begin{aligned}-\left\langle \frac{2e}{4\pi\epsilon_0} \frac{1}{r} \right\rangle &= -\frac{m}{2\hbar^2} \frac{4e^3}{(4\pi\epsilon_0)^2} \frac{1}{n^2} \\-\frac{2e}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle &= -\frac{m}{2\hbar^2} \frac{4e^3}{(4\pi\epsilon_0)^2} \frac{1}{n^2} \\\left\langle \frac{1}{r} \right\rangle &= -\frac{m}{\hbar^2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{n^2}.\end{aligned}$$

We know the Bohr radius is

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}.$$

Thus, the expectation value of $1/r$ for hydrogen is given by

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0 n^2}.$$

MOLECULAR FORCES

Consider a molecular system with N electrons (indexed by i and j), and M nuclei (indexed by α and β). The γ th nucleus's position will be defined as $\mathbf{R}_\gamma = \{X_\gamma, Y_\gamma, Z_\gamma\}$. The Hamiltonian is given by

$$\hat{H} = \hat{T} + \hat{V} + \sum_{i=1}^N \sum_{j>i} \frac{1}{\mathbf{r}_{ij}} - \sum_{i=1}^N \sum_{\alpha=1}^M \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \sum_{\alpha=1}^M \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}.$$

We will implement the Hellmann-Feynman theorem to obtain the x -component of the force applied to the nucleus indexed by γ .

$$\mathbf{F}_{x_\gamma} = - \left\langle \psi \left| \frac{\partial \hat{H}}{\partial X_\gamma} \right| \psi \right\rangle.$$

We start by calculating the derivative of \hat{H} with respect to the nuclear coordinate X_γ ,

$$\begin{aligned}\frac{\partial \hat{H}}{\partial X_\gamma} &= \frac{\partial}{\partial X_\gamma} \left(- \sum_{i=1}^N \sum_{\alpha=1}^M \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \sum_{\alpha=1}^M \sum_{\beta > \alpha} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \right) \\ &= -Z_\gamma \left(\sum_{i=1}^N \frac{x_i - X_\gamma}{|\mathbf{r}_i - \mathbf{R}_\gamma|^3} - \sum_{\alpha \neq \gamma}^M \frac{Z_\alpha (X_\alpha - X_\gamma)}{|\mathbf{R}_\alpha - \mathbf{R}_\gamma|^3} \right).\end{aligned}$$

Finally, taking the inner-product results in

$$\begin{aligned}\mathbf{F}_{X_\gamma} &= - \left\langle \psi \left| -Z_\gamma \left(\sum_{i=1}^N \frac{x_i - X_\gamma}{|\mathbf{r}_i - \mathbf{R}_\gamma|^3} - \sum_{\alpha \neq \gamma}^M \frac{Z_\alpha (X_\alpha - X_\gamma)}{|\mathbf{R}_\alpha - \mathbf{R}_\gamma|^3} \right) \right| \psi \right\rangle \\ &= Z_\gamma \left(\int \frac{x - X_\gamma}{|\mathbf{r} - \mathbf{R}_\gamma|^3} \rho(\mathbf{r}) d\mathbf{r} - \sum_{\alpha \neq \gamma}^M \frac{Z_\alpha (X_\alpha - X_\gamma)}{|\mathbf{R}_\alpha - \mathbf{R}_\gamma|^3} \right),\end{aligned}$$

where $\rho(\mathbf{r})$ is the electron density.

LONG-RANGE INTERACTION FORCES FOR SEPARATED HYDROGEN

The force of interaction between two well-separated hydrogen atoms aligned along the z-axis is given by

$$E = C_6 R^{-6} + C_8 R^{-8} + C_{10} R^{-10} + \dots,$$

which is derived from a second-order perturbation theory treatment of the interaction. From here, we may use the Hellmann-Feynman theorem to obtain the z-direction contribution to the force of nucleus γ :

$$\mathbf{F}_\gamma = -\frac{\partial E}{\partial R} = -6C_6 R^{-7} - 8C_8 R^{-9} - 10C_{10} R^{-11} - \dots.$$

However, obtaining the C_i coefficients is non-trivial.

J. Hirschfelder, M. Eliason, *Electrostatic Hellmann-Feynman Theorem Applied to the Long-Range Interaction of Two Hydrogen Atoms*, J. Chem. Phys. **47**, 3 (1967)

A. D. Becke, E. R. Johnson, *Exchange-hole dipole moment and the dispersion interaction revisited*, J. Chem. Phys. **127**, 154108 (2007)

The Hamiltonian for this system is given by

$$\hat{H} = H_0 + V,$$

where the zeroth-order Hamiltonian H_0 and perturbation V are given by

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_\gamma|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_\beta|},$$
$$V = -\frac{1}{|\mathbf{r}_1 - \mathbf{R}_\beta|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_\gamma|} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} + \frac{1}{|\mathbf{R}_\beta - \mathbf{R}_\gamma|}.$$

The force on nucleus γ is then

$$\mathbf{F}_\gamma = \left\langle \psi \left| \frac{\mathbf{r}_1 - \mathbf{R}_\gamma}{|\mathbf{r}_1 - \mathbf{R}_\gamma|^3} + \frac{\mathbf{r}_2 - \mathbf{R}_\gamma}{|\mathbf{r}_2 - \mathbf{R}_\gamma|^3} - \frac{\mathbf{R}_\beta - \mathbf{R}_\gamma}{|\mathbf{R}_\beta - \mathbf{R}_\gamma|^3} \right| \psi \right\rangle,$$

which agrees with the form that was calculated for molecular forces. The Hellmann-Feynman theorem determination of $\frac{\partial E^{(n)}}{\partial \mathbf{r}}$ will (typically¹) require the wavefunction through to n th order.

¹E. Steiner, *Electrostatic Hellmann-Feynman theorem applied to long-range interatomic forces. The hydrogen molecule*, J. Chem. Phys. **59**, 5 (1973)

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THE GEOMETRY OPTIMIZATION LOOP

```
1 Function SCF()
2 ! The SCF loop
3 !     Input: Geometry (G)
4 !     Output: Electron Density (rho), Energy (E)
5 Function HF()
6 ! The Hellmann-Feynman method for calculating forces
7 !     Input: Geometry (G), Electron Density (rho)
8 !     Output: Forces (F)
9 Function GOPT()
10 ! The Geometry Optimization function
11 !     Input: Geometry (G) , Forces (F)
12 !     Output: Geometry (G)
13
14 i = 0
15 G[i] = !User input
16
17 ( rho[i] , E[i] ) = SCF( G[i] )
18 F[i] = HF( G[i] , rho[i] )
19
20 While(F[i] < eps) !Some small threshold
21 {
22     i++
23     G[i] = GOPT( G[i-1] , F[i-1] )
24     ( rho[i] , E[i] ) = SCF( G[i] )
25     F[i] = HF( G[i] , rho[i] )
26 }
27 Return ( G[i] , rho[i] , E[i] )
```

WHERE IN THE QE ARE THE FORCES CALCULATED?

`forces.f90` is the driver subroutine that computes the forces acting on the atoms. The complete expression of the forces contains four parts, which are computed by different routines:

- `force_lc`: local contribution to the forces
- `force_cc`: contribution due to Non-Linear Core Correction (NLCC)
- `force_ew`: contribution due to the electrostatic Ewald term
- `force_us`: contribution due to the non-local potential
- `force_corr`: correction term for incomplete self-consistency
- `force_hub`: contribution due to the Hubbard term
- `force_london`: semi-empirical correction for dispersion forces
- `force_d3`: Grimme-D3 (DFT-D3) correction to dispersion forces

After all the force contributions are calculated, they're summed.

```
1 DO ipol = 1, 3
2   sumfor = 0.D0
3   DO na = 1, nat
4     force(ipol,na) = force(ipol,na) + &
5       forcenl(ipol,na) + &
6       forceion(ipol,na) + &
7       forcelc(ipol,na) + &
8       forcecc(ipol,na) + &
9       forceh(ipol,na) + &
10      forcescc(ipol,na)
11      IF ( llondon ) force(ipol,na) = force(ipol,na) + force_disp(ipol,na)
12      IF ( ldftd3 )  force(ipol,na) = force(ipol,na) + force_d3(ipol,na)
13      IF ( lxdm )    force(ipol,na) = force(ipol,na) + force_disp_xdm(ipol,na)
14      IF ( ts_vdw )  force(ipol,na) = force(ipol,na) + 2.0_dp*FtsvdW(ipol,na)
15      IF ( tefield ) force(ipol,na) = force(ipol,na) + forcefield(ipol,na)
16      IF ( gate )    force(ipol,na) = force(ipol,na) + forcegate(ipol,na)
17      IF ( lefield)  force(ipol,na) = force(ipol,na) + forces_bp_efield(ipol,na)
18      IF ( do_comp_mt)force(ipol,na) = force(ipol,na) + force_mt(ipol,na)
19      sumfor = sumfor + force(ipol,na)
20   ENDDO
21 .
22 .
23 .
24 ENDDO
```

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- Electronic-structure theory software will calculate the forces on each atom in the system and try to optimize the system's geometry.
- The system will optimize its geometry until it settles into a local minimum in the potential energy surface.
- Forces within molecular systems are conservative, and may be calculated with the Hellmann-Feynman theorem.
- A thorough treatment of the forces is essential, because without it, our simulated chemical systems could relax to an incorrect geometry.
- We should consider the Quantum ESPRESSO developers as saints for making their code open-source.

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ACKNOWLEDGEMENTS

- Erin Johnson
- Joe Weatherby
- Tilas Kabengele
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QUESTIONS?

WANT MY SLIDES?



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