Center for
Molecular
Modeling

# Computational Materials Physics

Department of
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## quantum forces

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http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

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## Quantum forces

The Born-Oppenheimer hamiltonian for our solid was:

$$
\begin{aligned}
H = & \cancel{-\sum_i \frac{\nabla^2}{M_i}} \\
& -\sum_i \frac{\nabla^2}{m_i} \\
& -\sum_{i,j} \frac{(eZ_i)\ e}{\left|\vec{R}_i - \vec{r}_j\right|} \\
& +\frac{1}{2}\sum_{i\neq j} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} \\
& +\frac{1}{2}\sum_{i\neq j} \frac{(eZ_i)(eZ_j)}{\left|\vec{R}_i - \vec{R}_j\right|}
\end{aligned}
$$

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## Quantum forces

For atoms/nuclei with free parameters, it makes sense to ask:
"which force do they feel when they are displaced?"

Classical force associated with the generalized coordinate q:

$$F_q = \dot{p} = -\frac{\partial \mathcal{H}}{\partial q}$$

Quantum version (given our context, we take as generalized coordinate a displacement of one particular nucleus along the z-axis) :

$$F_z = \dot{p} = -\frac{\partial \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle}{\partial z}$$

## Quantum forces

$$\frac{\partial \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle}{\partial z} = \left\langle \frac{\partial\Psi}{\partial z}\right|\hat{\mathcal{H}}|\Psi\rangle + \langle\Psi|\frac{\partial\hat{\mathcal{H}}}{\partial z}|\Psi\rangle + \langle\Psi|\hat{\mathcal{H}}\left|\frac{\partial\Psi}{\partial z}\right\rangle$$

We need to know how the wave function changes
if that particular nucleus moves: complicated !

We need to know how the Hamiltonian changes
if that particular nucleus moves: straightforward !

## Quantum forces

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$$\begin{aligned} H = & -\xcancel{\sum_i \frac{\nabla^2}{M_i}} \\ & -\xcancel{\sum_i \frac{\nabla^2}{m_i}} \\ & -\sum_{i,j}\frac{(eZ_i)\ e}{|\vec{R}_i-\vec{r}_j|} \\ & +\xcancel{\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}} \\ & +\frac{1}{2}\sum_{i\neq j}\frac{(eZ_i)(eZ_j)}{|\vec{R}_i-\vec{R}_j|} \end{aligned}$$

Does not appear anyway

Does not depend on nuclear
positions

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

(equation from http://en.wikipedia.org/wiki/Hellmann-Feynman_theorem)

## Quantum forces

So far the easy part. What about the wave function terms?

$$\frac{\partial \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle}{\partial z} = \cancel{\left\langle \frac{\partial\Psi}{\partial z}\right|\hat{\mathcal{H}}|\Psi\rangle} + \langle\Psi|\frac{\partial\hat{\mathcal{H}}}{\partial z}|\Psi\rangle + \cancel{\langle\Psi|\hat{\mathcal{H}}\left|\frac{\partial\Psi}{\partial z}\right\rangle}$$

Hellmann-Feynman theorem:

$$\frac{\partial \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle}{\partial z} = \langle\Psi|\frac{\partial\hat{\mathcal{H}}}{\partial z}|\Psi\rangle$$

We don't need to know at all
how the wave function changes…!

By evaluating the hamiltonian $Z_\gamma\sum_{i=1}^{N}\frac{x_i-X_\gamma}{|\mathbf{r}_i-\mathbf{R}_\gamma|^3} - Z_\gamma\sum_{\alpha\neq\gamma}^{M}Z_\alpha\frac{X_\alpha-X_\gamma}{|\mathbf{R}_\alpha-\mathbf{R}_\gamma|^3}.$
in the ground state wave function, we know the z-component
of the force on this particular atom.

## Quantum forces

Verbal interpretation :

"The force on an atom is equal to
the electrostatic force on its nucleus."

Hellmann-Feynman theorem:

$$\frac{\partial \langle\Psi|\,\hat{\mathcal{H}}\,|\Psi\rangle}{\partial z} = \langle\Psi|\,\frac{\partial\hat{\mathcal{H}}}{\partial z}\,|\Psi\rangle$$

We don't need to know at all
how the wave function changes…!

By evaluating the hamiltonian $Z_\gamma \sum_{i=1}^{N} \frac{x_i - X_\gamma}{|\mathbf{r}_i - \mathbf{R}_\gamma|^3} - Z_\gamma \sum_{\alpha\neq\gamma}^{M} Z_\alpha \frac{X_\alpha - X_\gamma}{|\mathbf{R}_\alpha - \mathbf{R}_\gamma|^3}$.
in the ground state wave function, we know the z-component of the force on this particular atom.