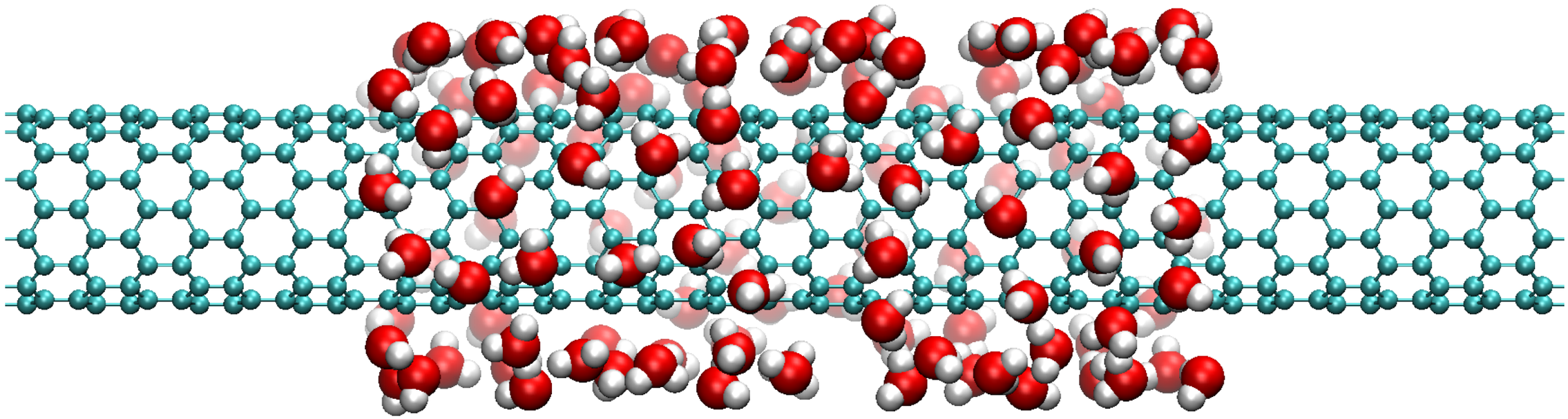
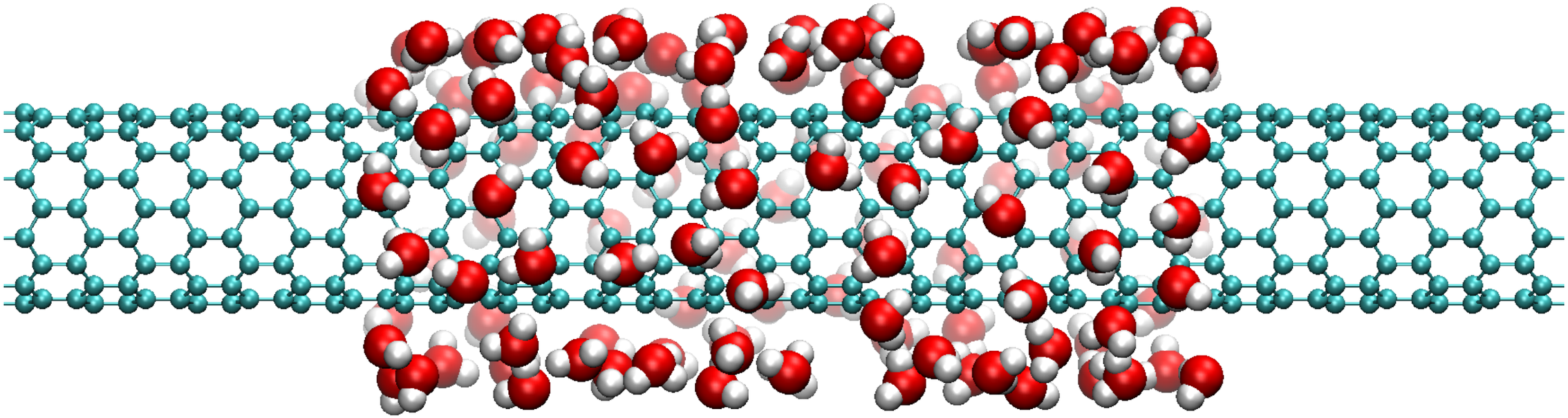
Charge transfer in Carbon Nanotubes (?)

ESDG 13 Feb 2013

Robert Bell, Arash Mostofi





"H_2O molecules can be adsorbed on the nanotubes and act like electron donors"

"The electronic properties of [nanotubes] can be deeply modified by [...] minute quantities of H_2O."

PRB **62** 15 (2000)

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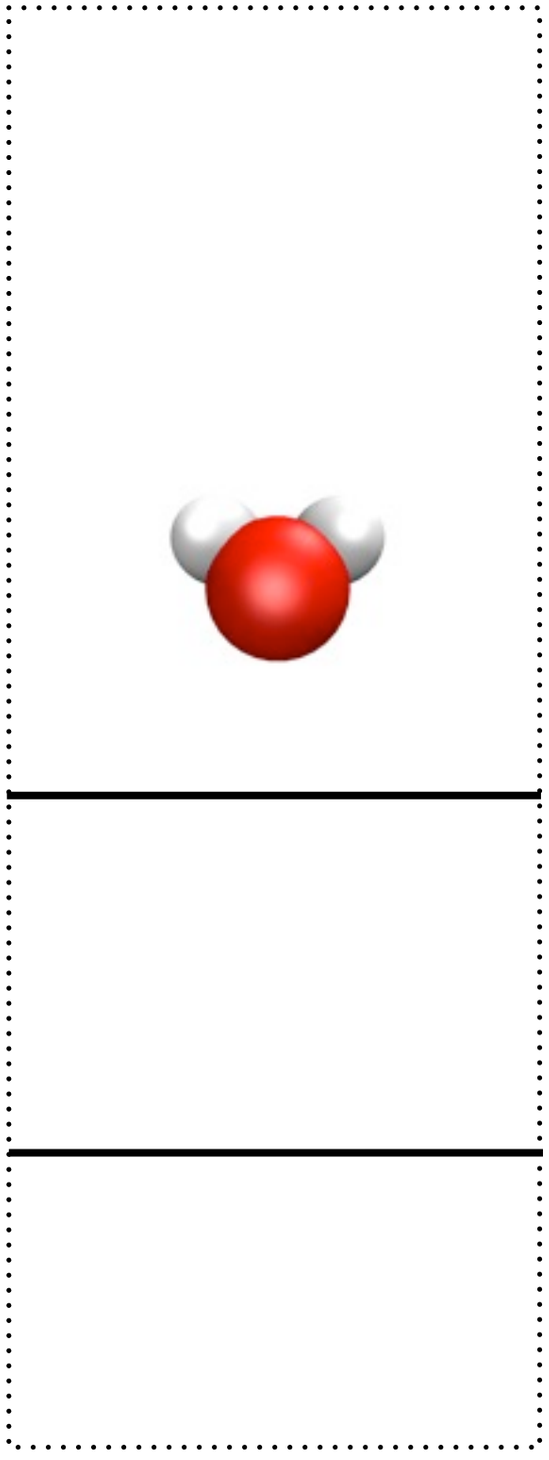
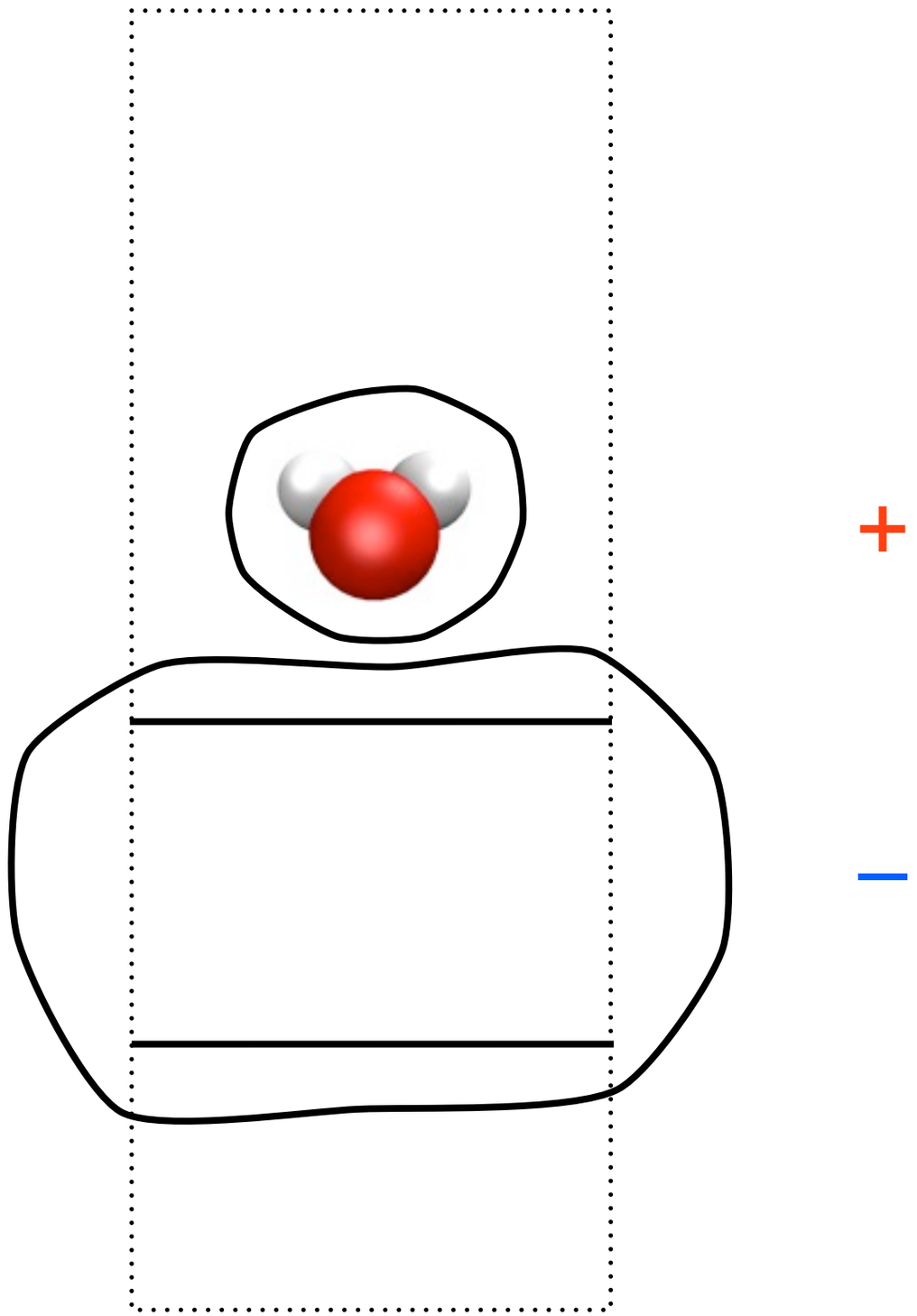
Charge transfer model (?)



PRB **62** 15 (2000)

Charge transfer model (?)

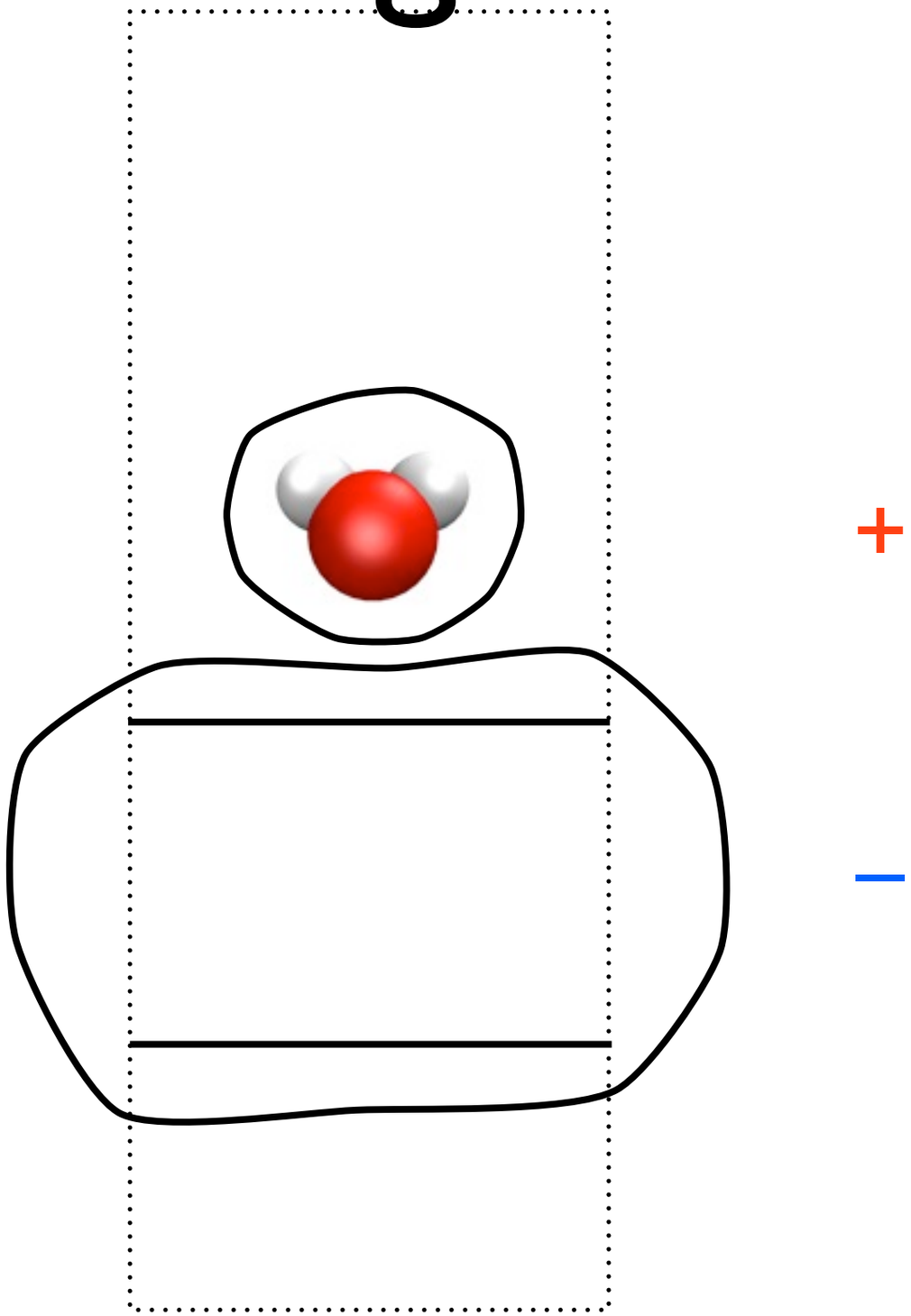


+

−

PRB **62** 15 (2000)

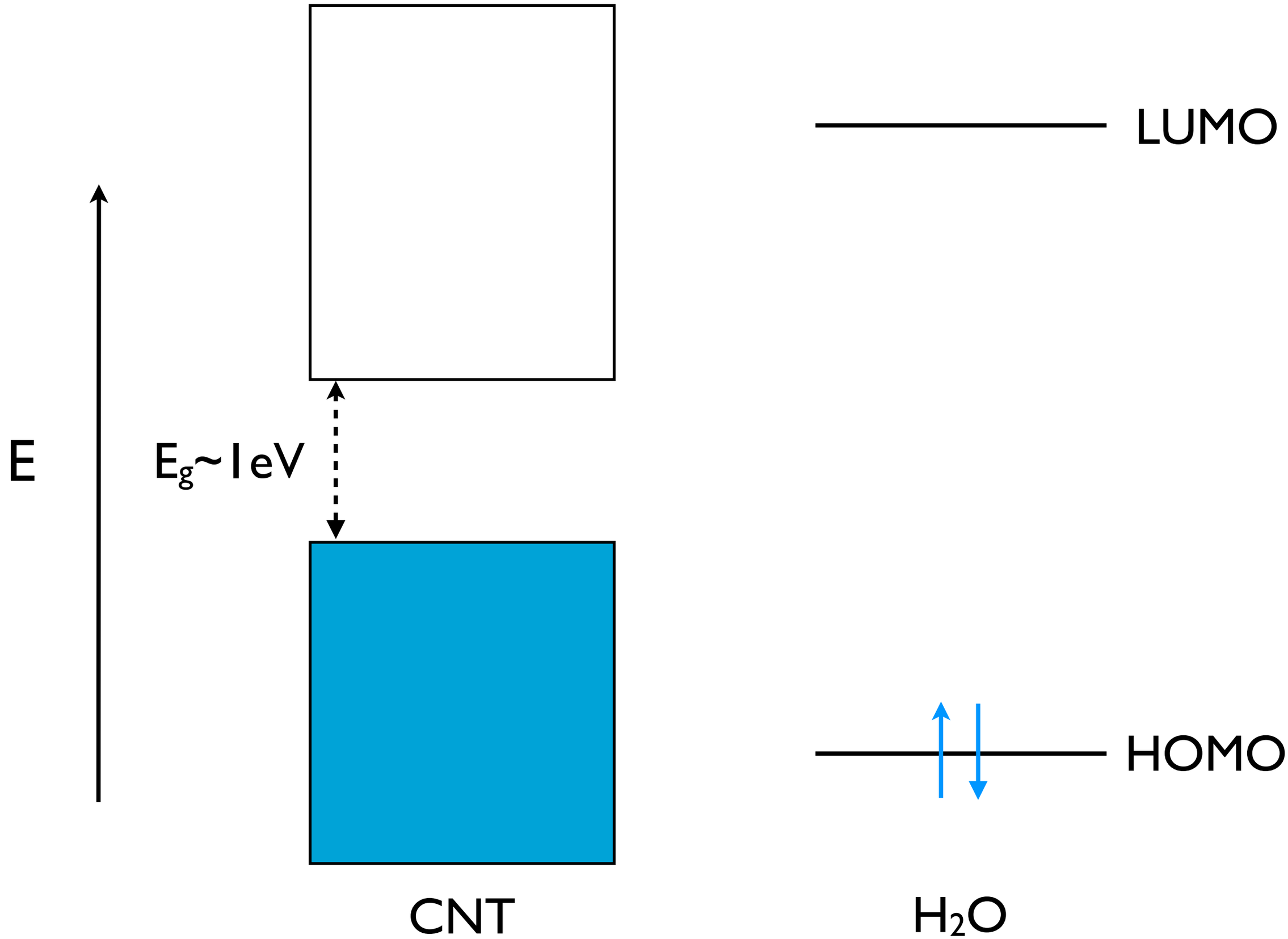
Charge transfer model (?)

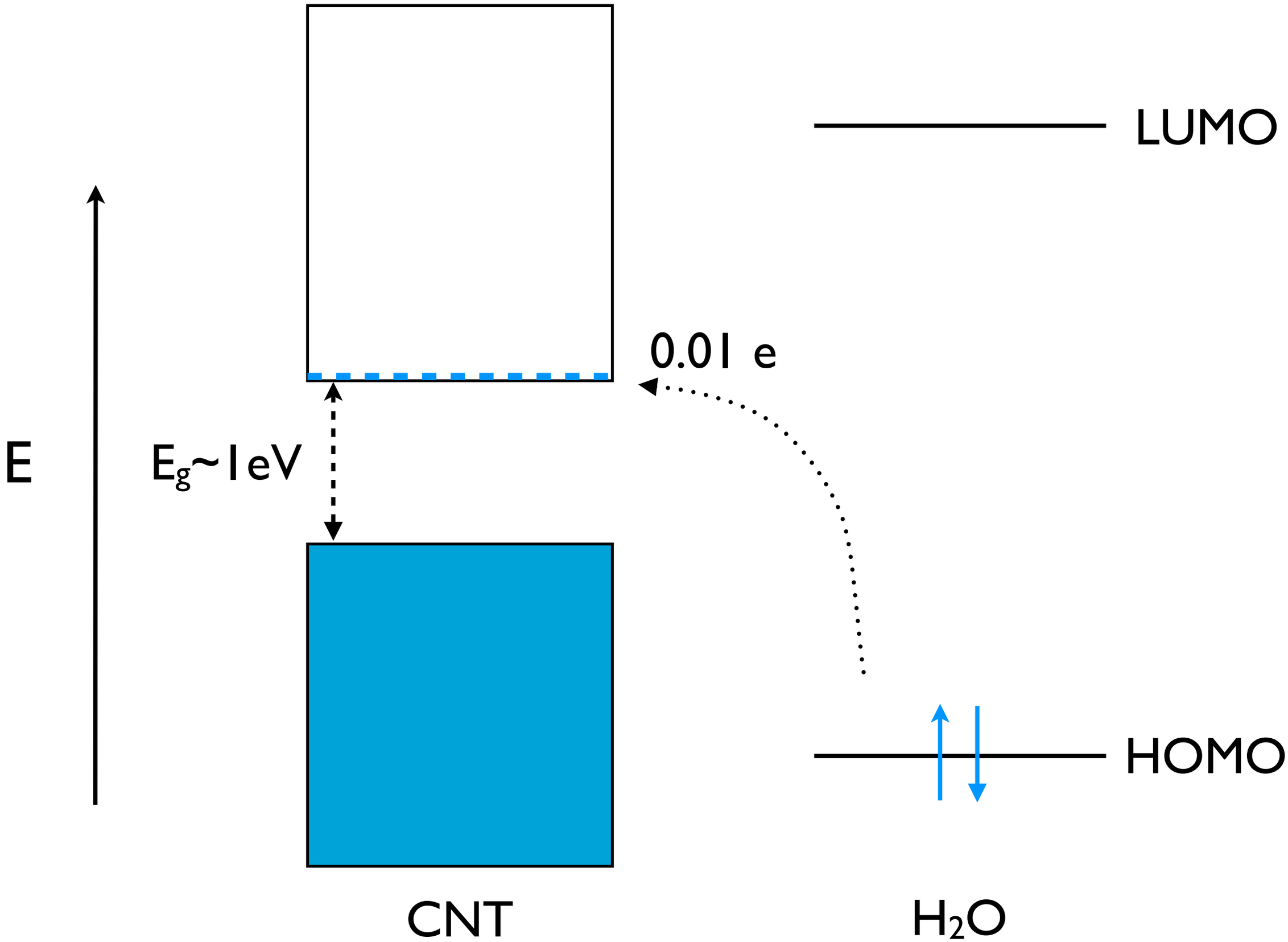


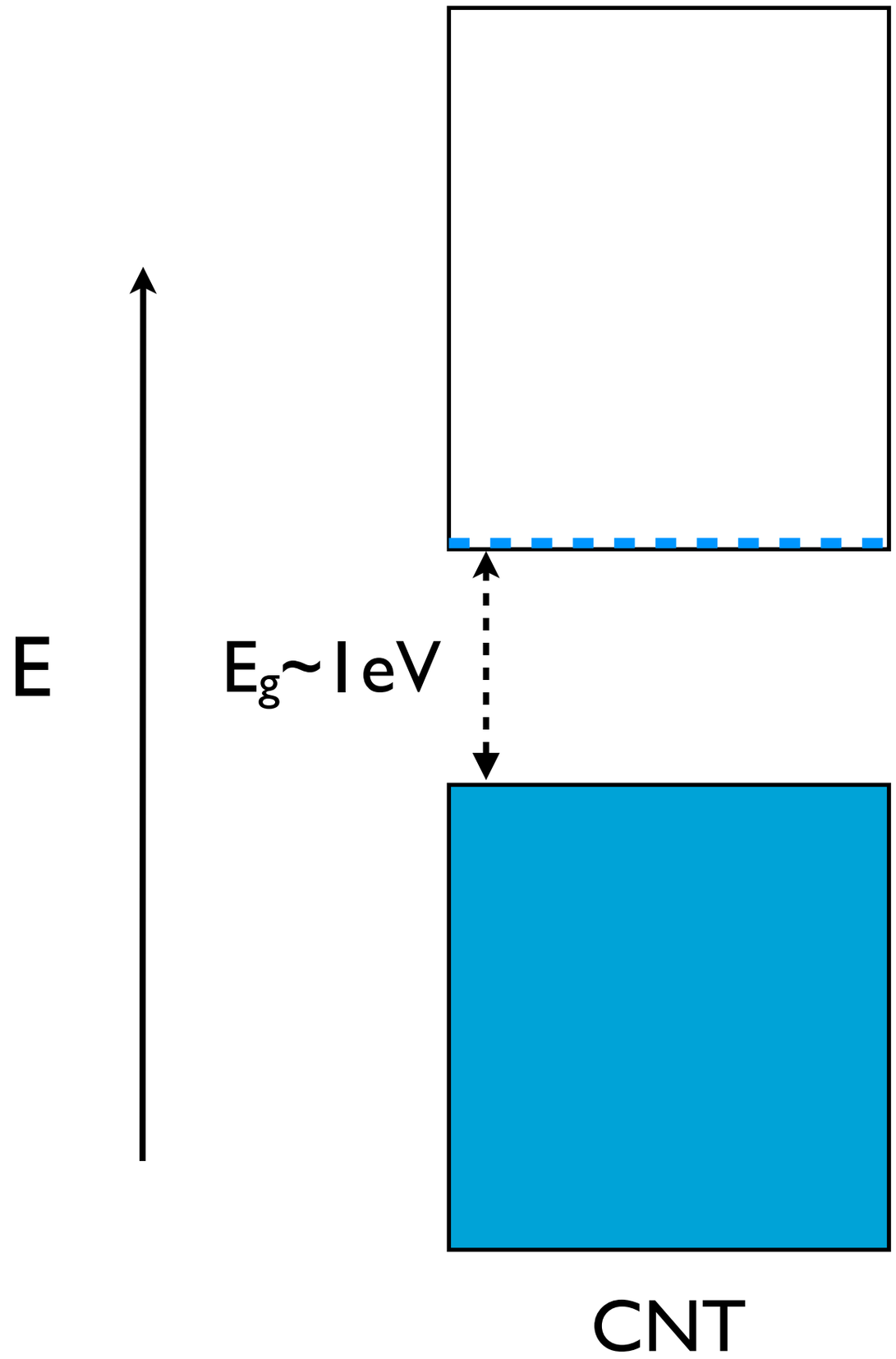
+

−

- Mulliken analysis to assign ionic partial charges
- Water net positive
- CNT net negative


LUMO
E
E_g~1eV
HOMO
CNT
H_2O


LUMO
0.01 e
E
E_g~1eV
CNT
H_2O
HOMO

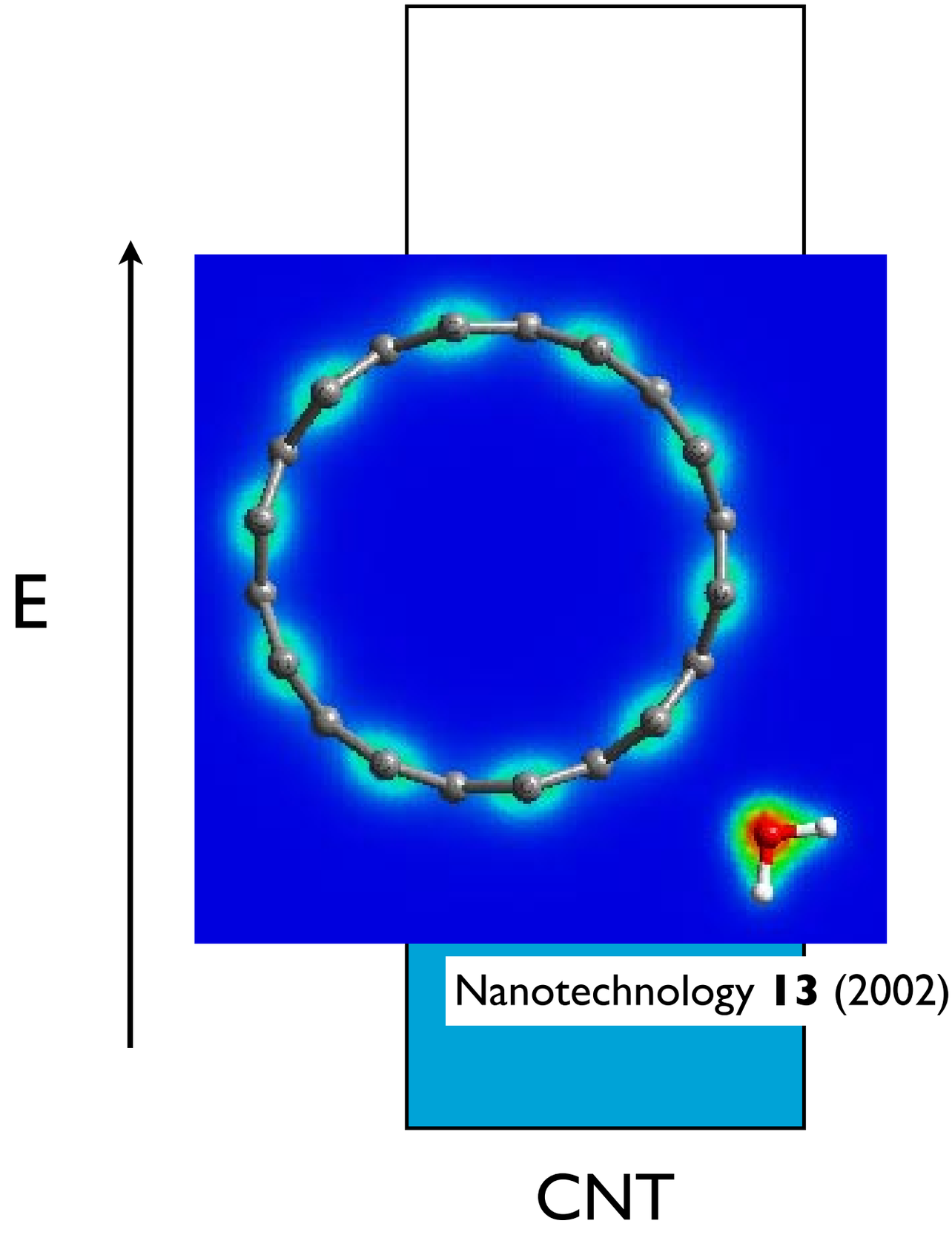


Expected observations:

- Strong interaction
- Modified bandstructure
- Delocalised electrons

Issues:

- Energy penalty
- Poor state alignment
- Scattering effect



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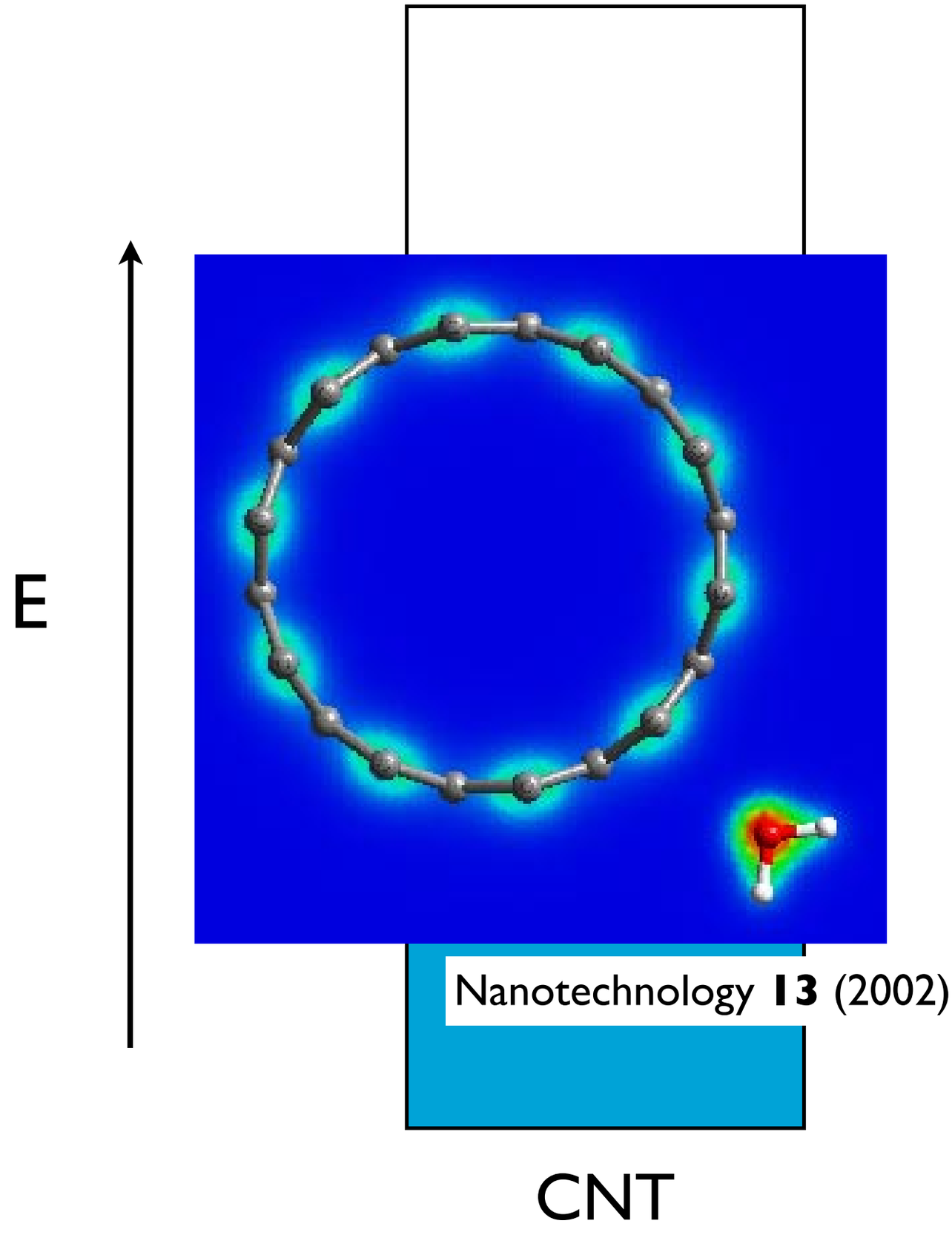

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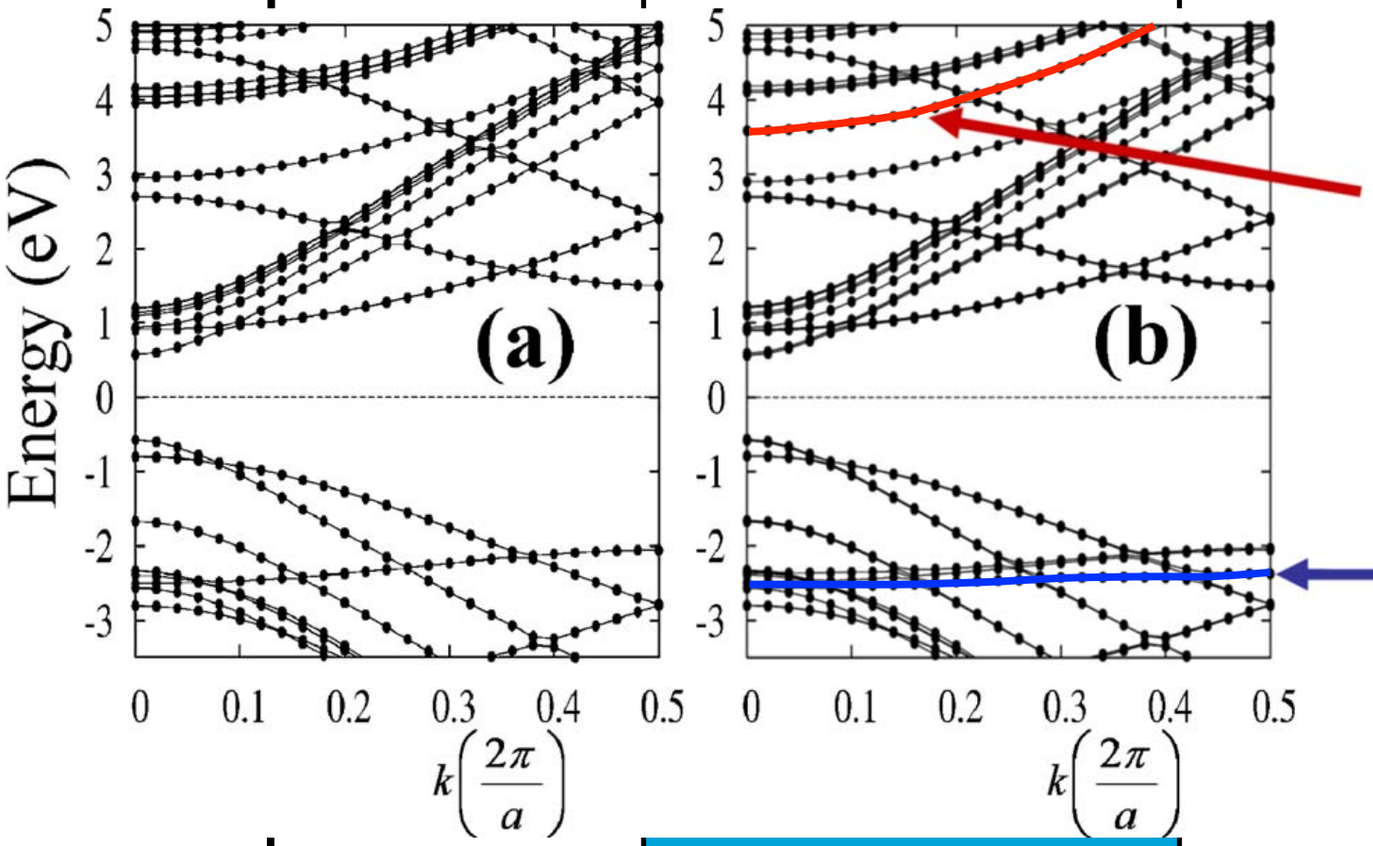

App. Phys. Lett **89** 243110 (2006)

CNT

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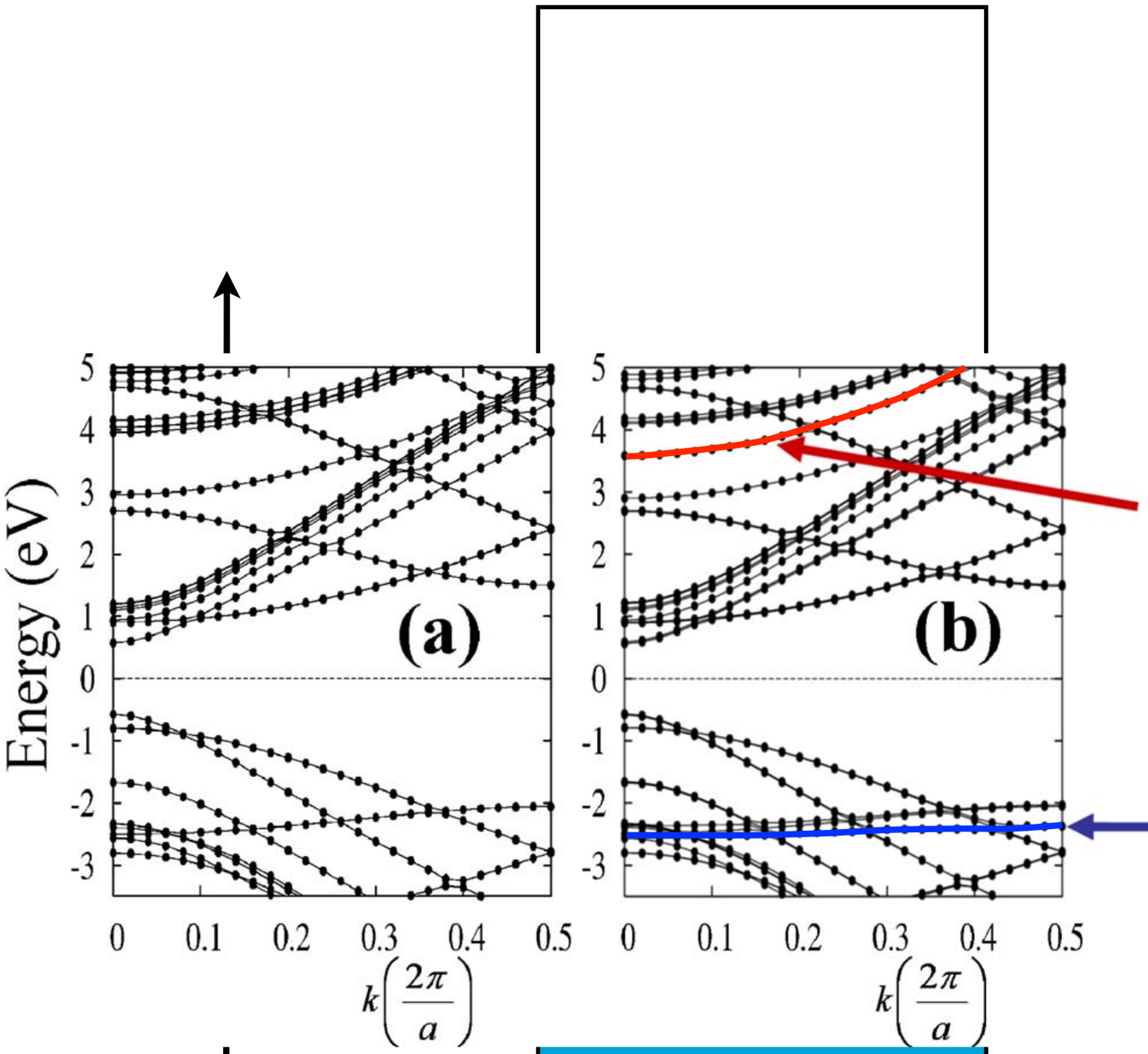

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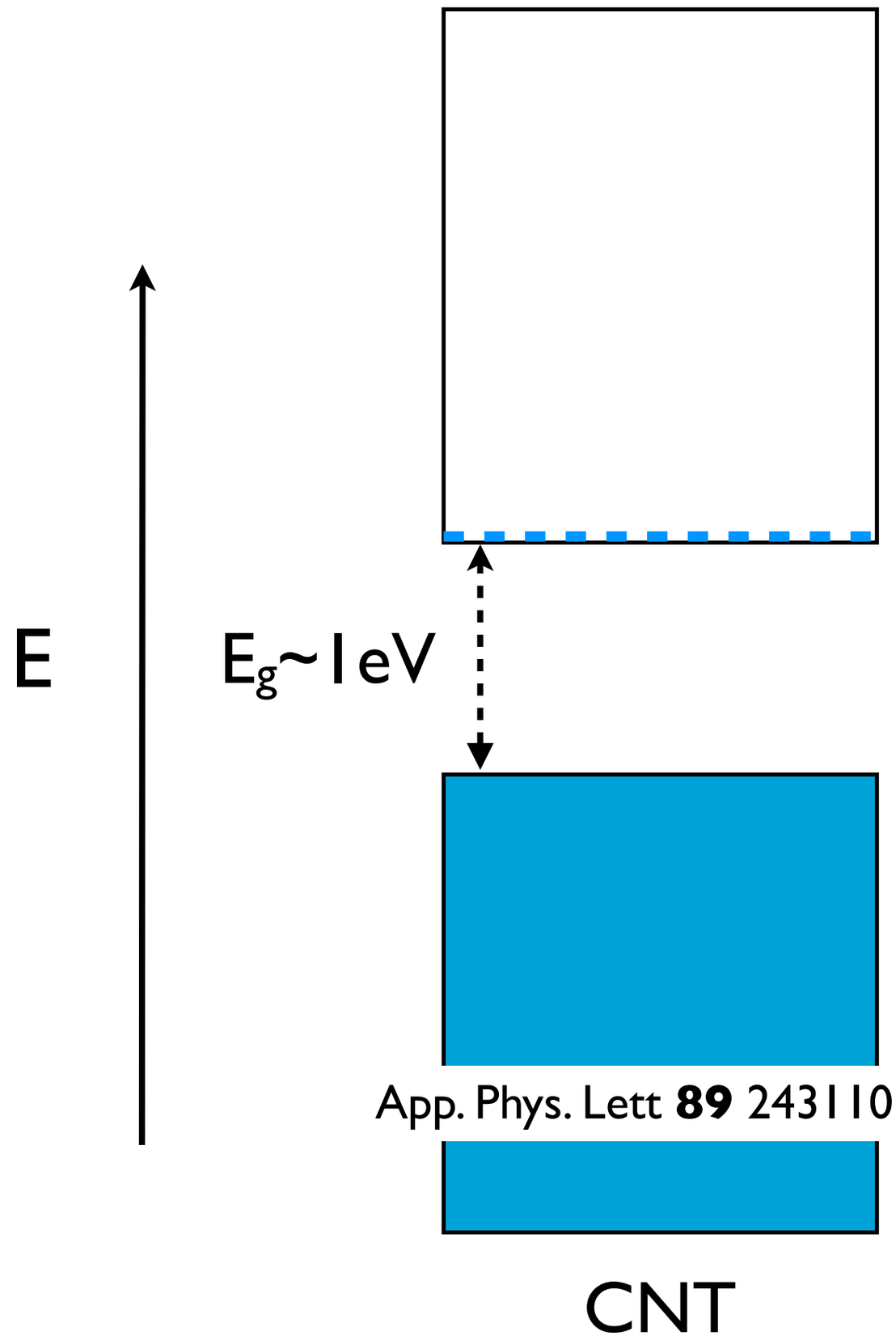

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~~Modified bandstructure~~

Delocalised electrons

Issues:

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Poor state alignment

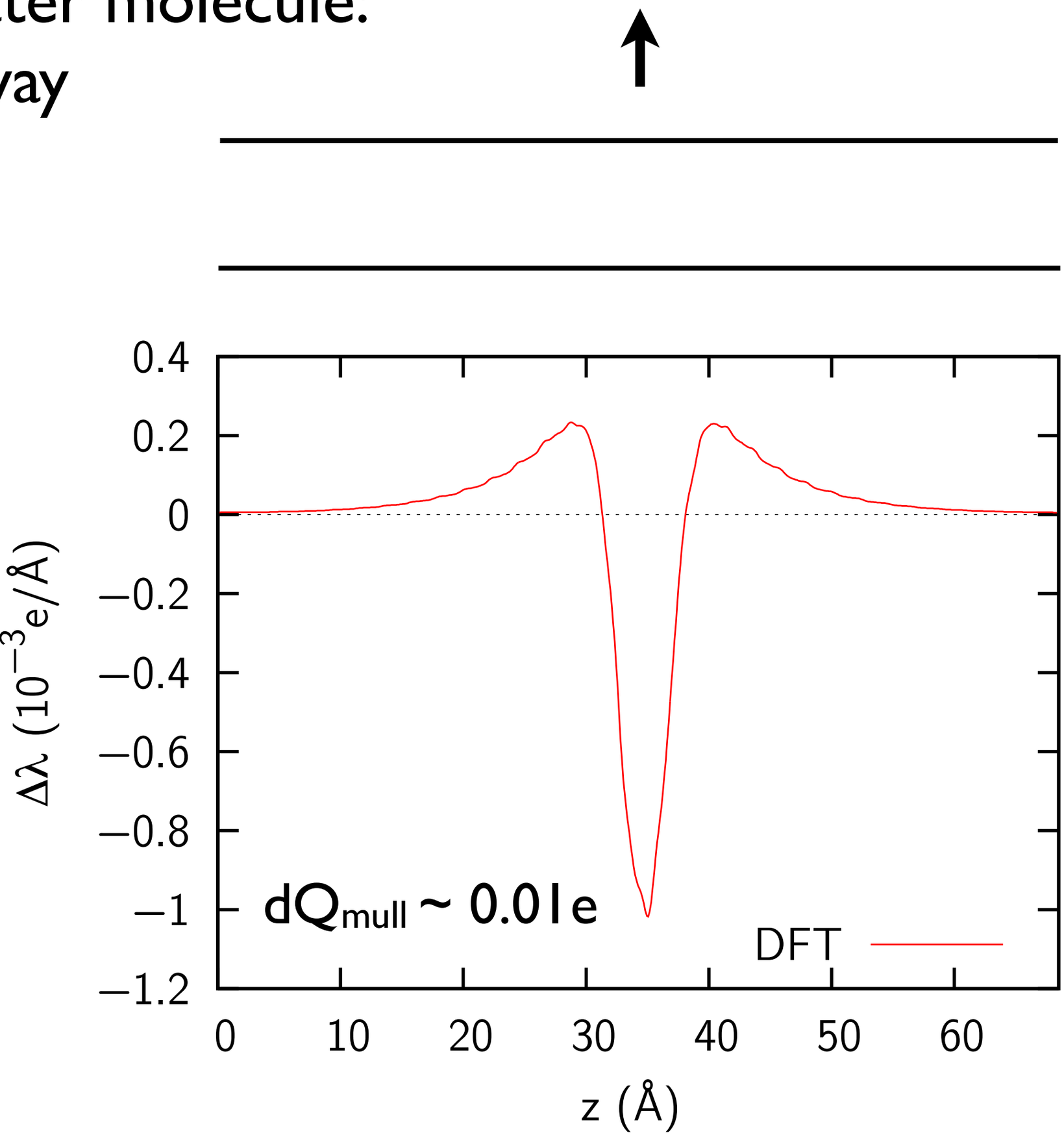
Scattering effect

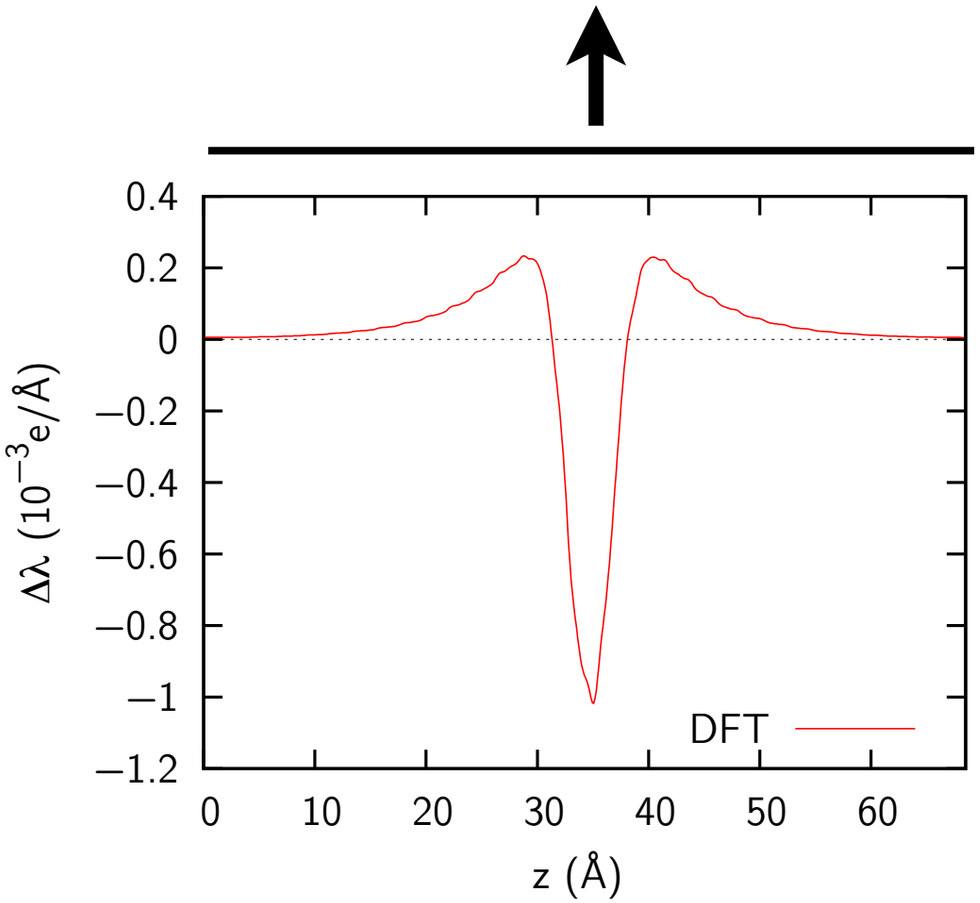
67.5 Angstrom

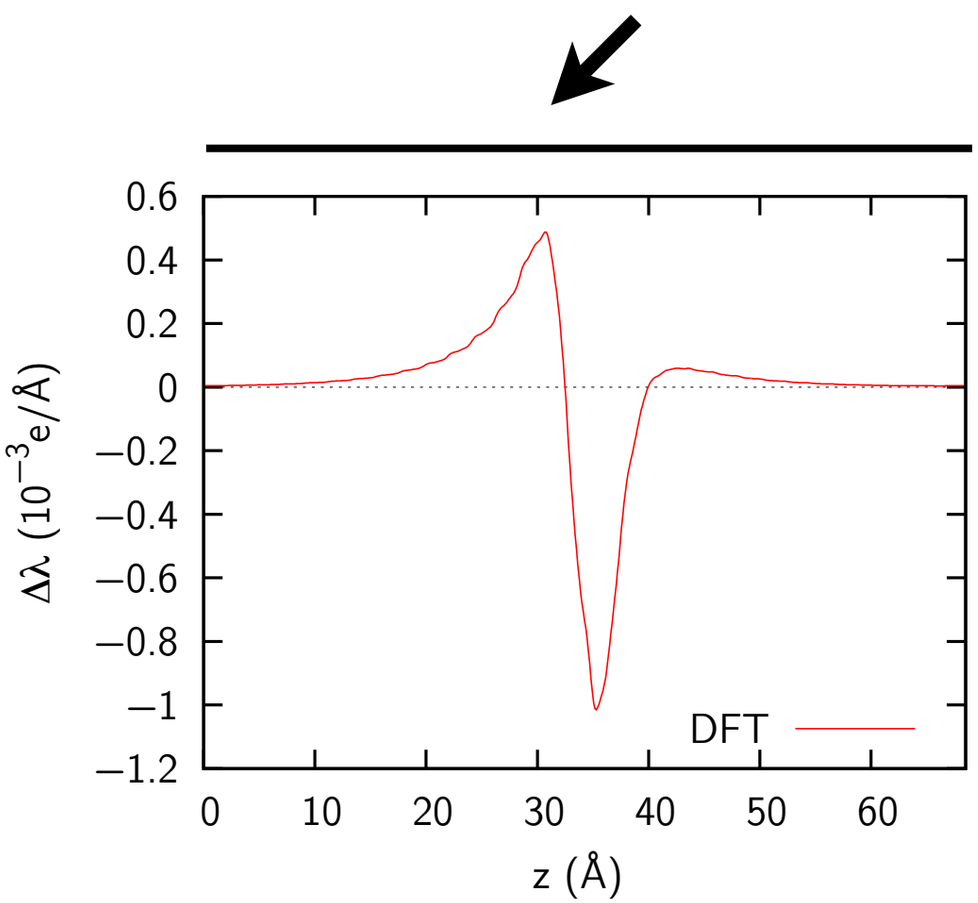
$$\Delta\lambda(z) = \int \Delta n(\vec{r})\, dx\, dy$$

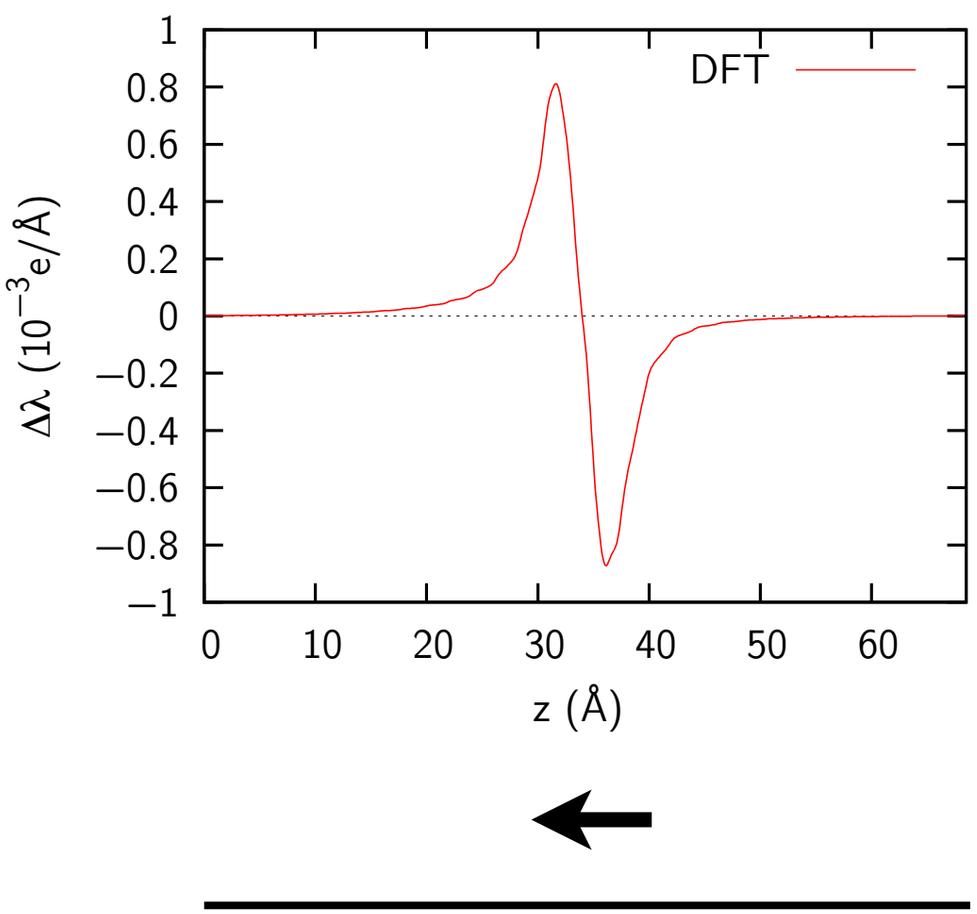
$$= \int \left[n_{CNT+H_2O}(\vec{r}) - n_{CNT}(\vec{r}) - n_{H_2O}(\vec{r}) \right] dx\, dy.$$

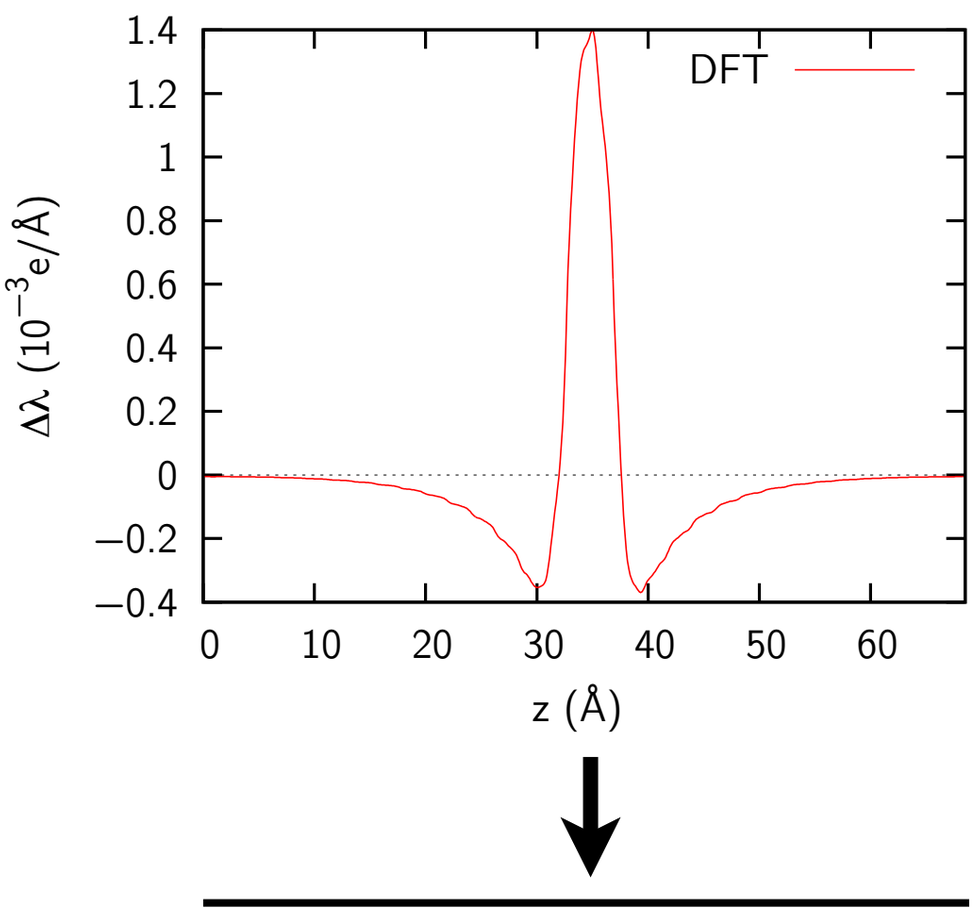
Single water molecule: dipole away

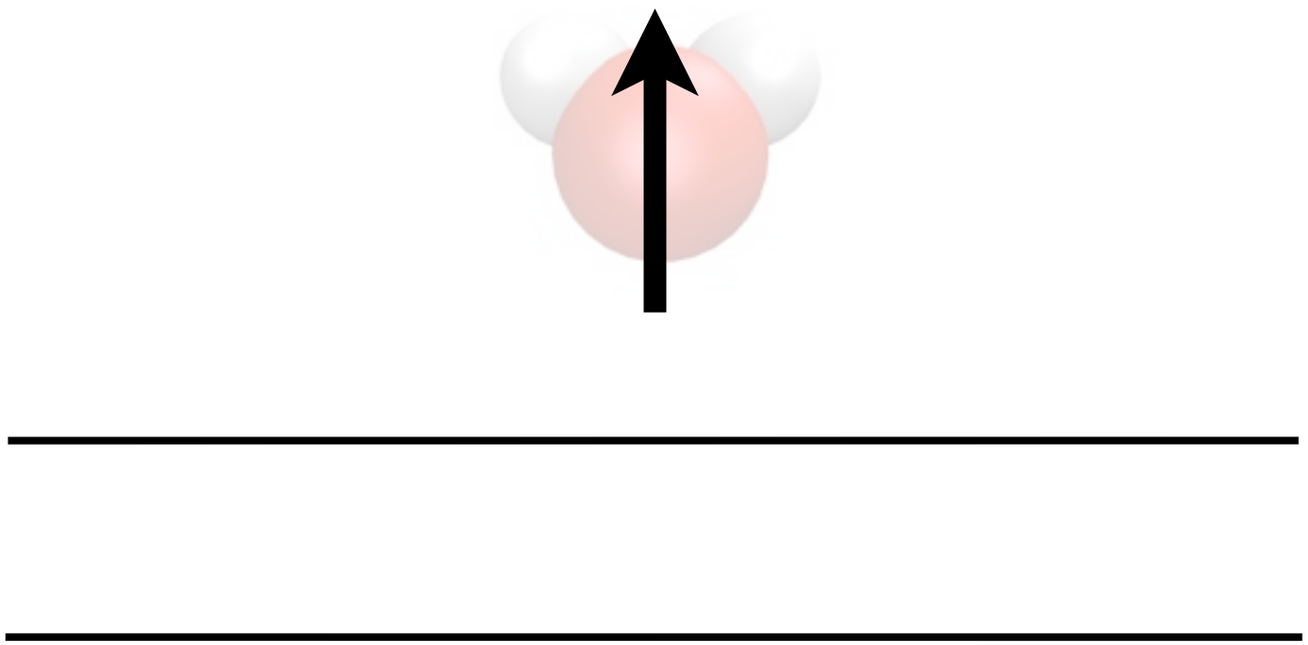


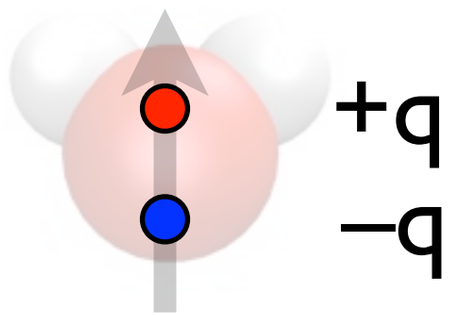

0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
−1.2
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT


0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
−1.2
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT


1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT


1.4
1.2
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT



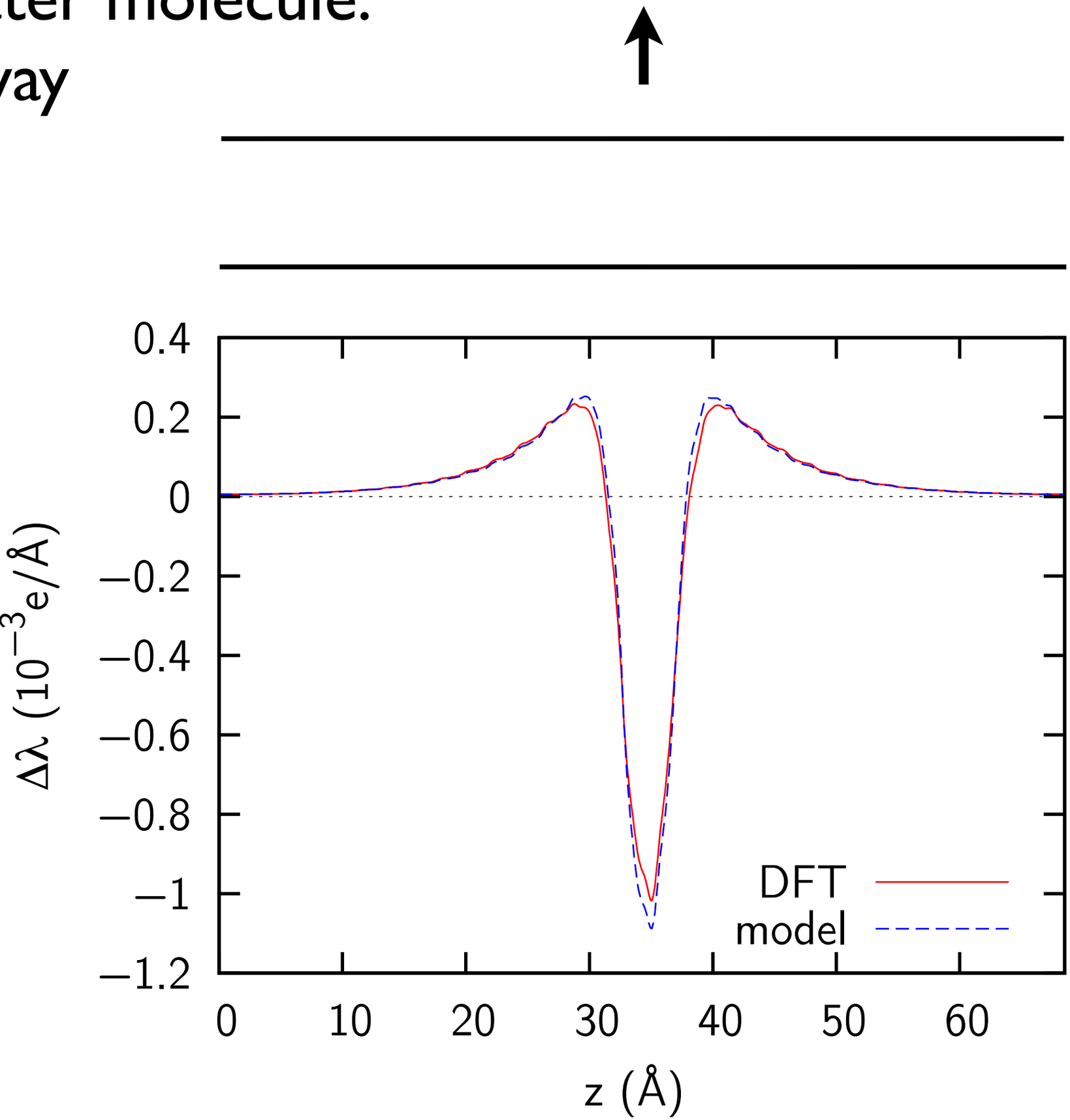


$$\delta V_{\rm loc}(\vec{r}) = \frac{q}{|\vec{r}-\vec{r}_+|} - \frac{q}{|\vec{r}-\vec{r}_-|}$$

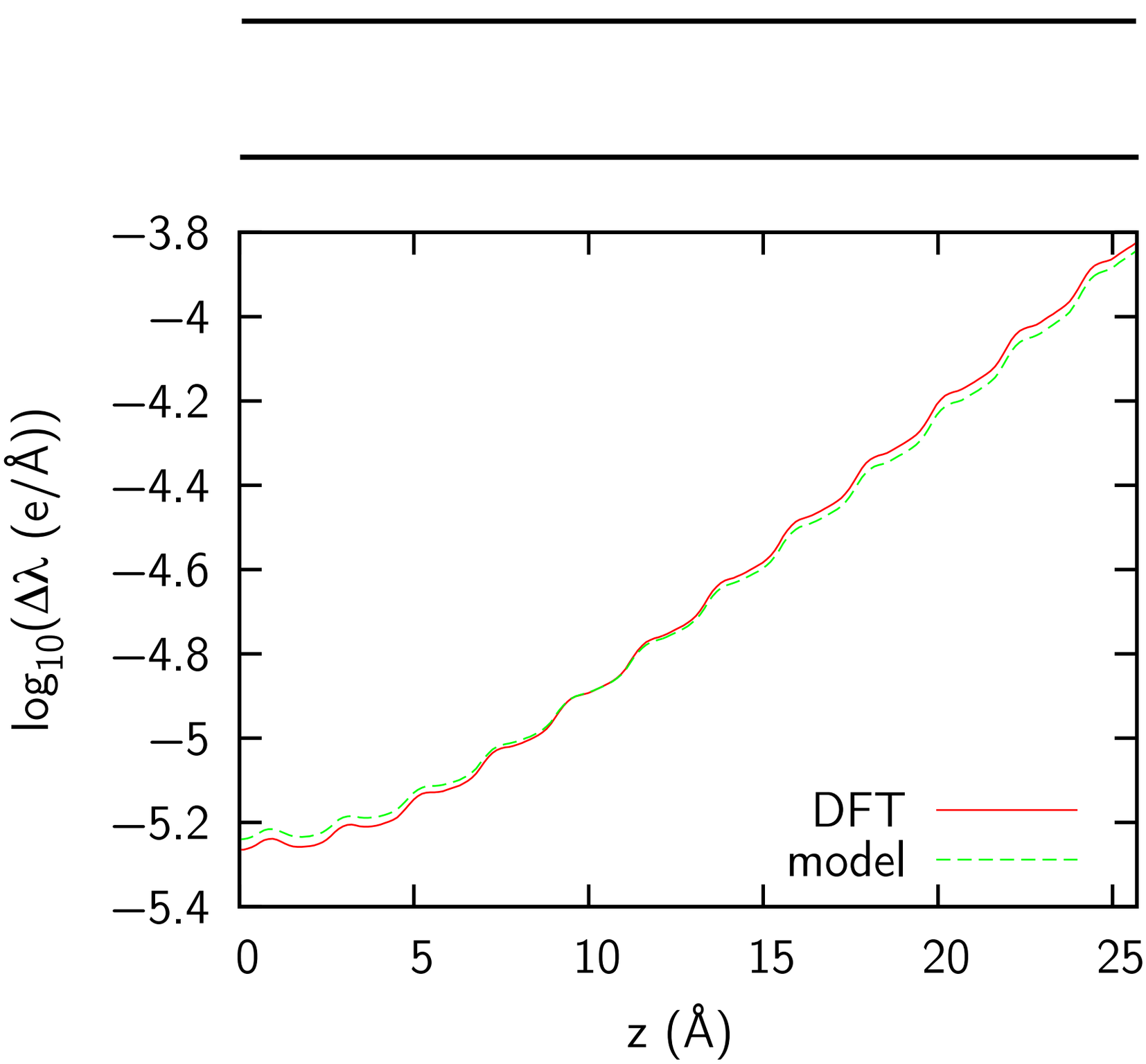
$$\delta V_{\rm loc}(\vec{g}) = q\Big[\frac{e^{i\vec{g}\cdot\vec{r}_+}}{g^2} - \frac{e^{i\vec{g}\cdot\vec{r}_-}}{g^2}\Big]$$

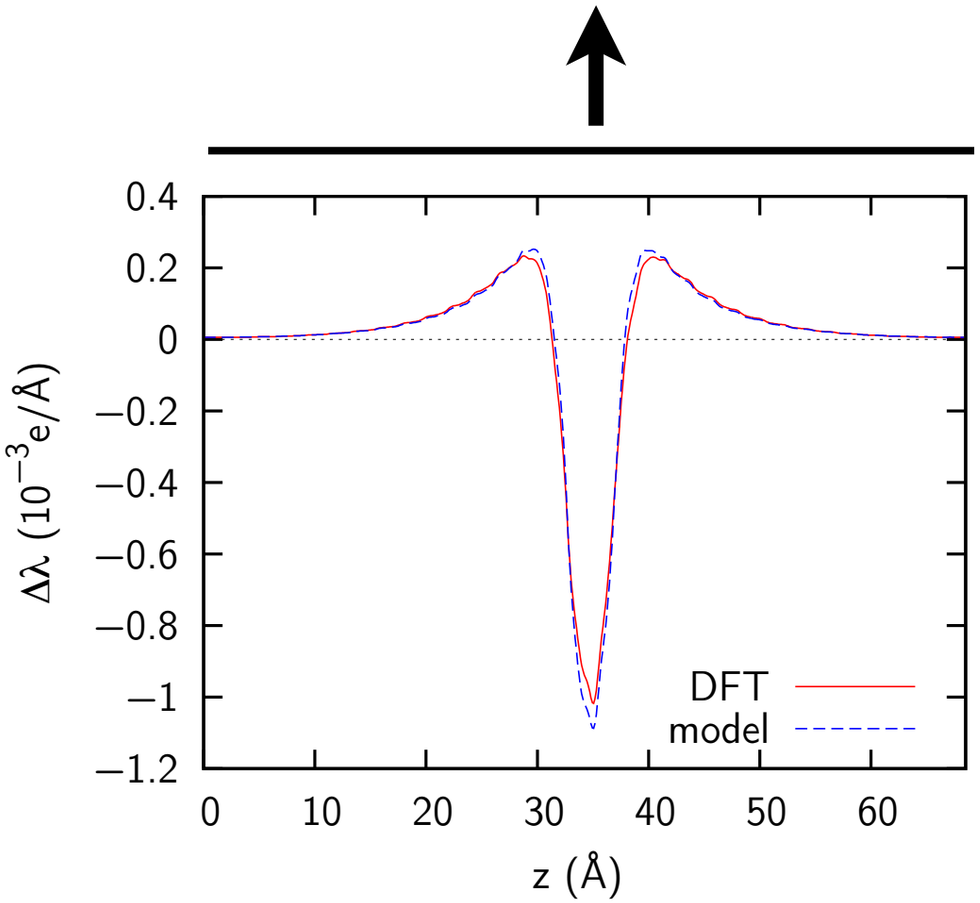
- No electrons added
- Exact long-range interaction
- Parameter free

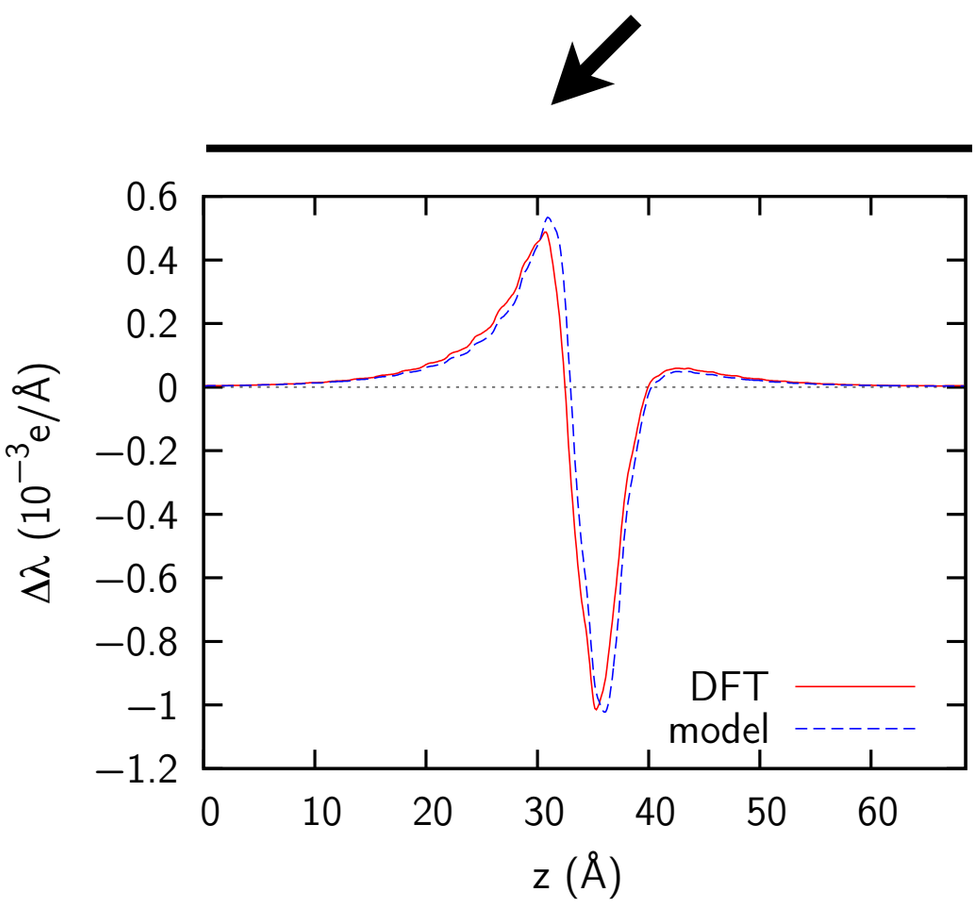
Single water molecule: dipole away

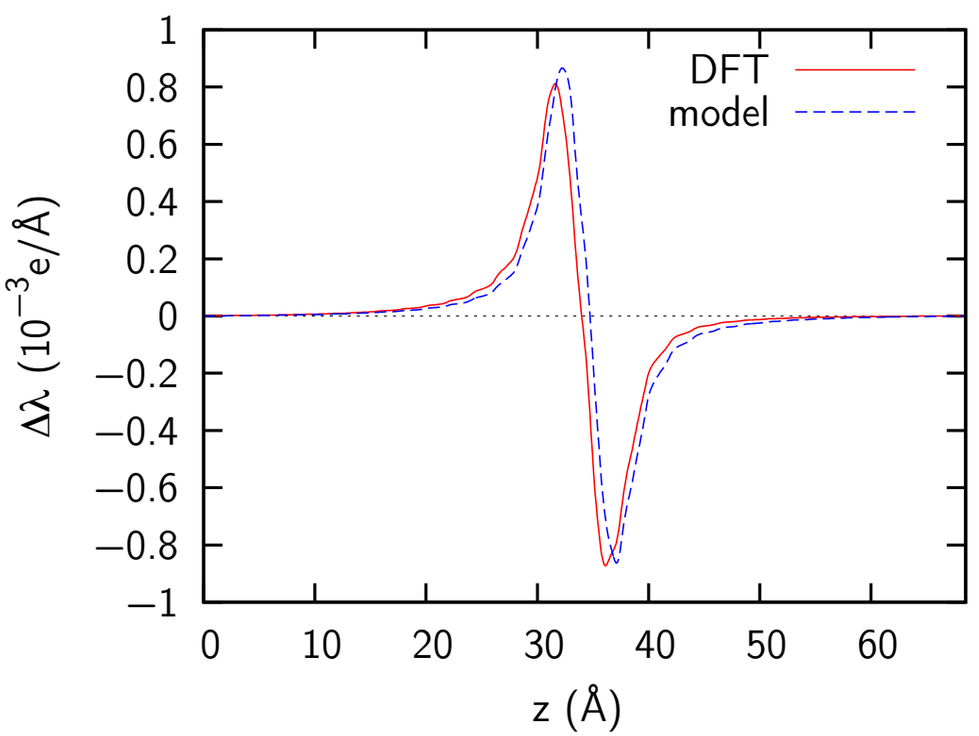


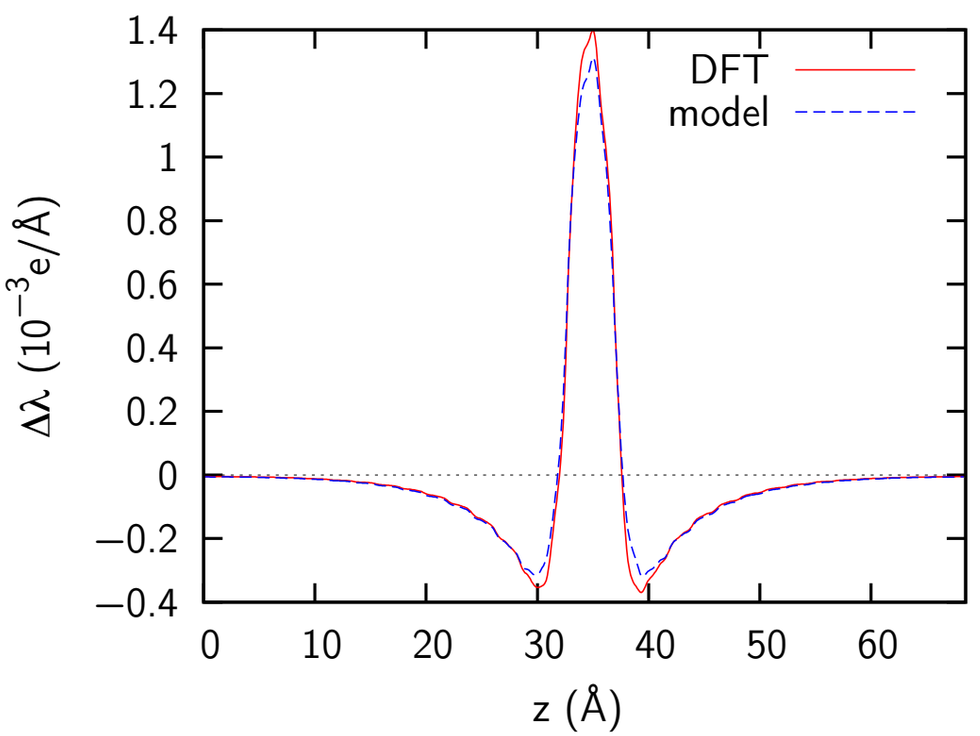
Single water molecule: dipole away

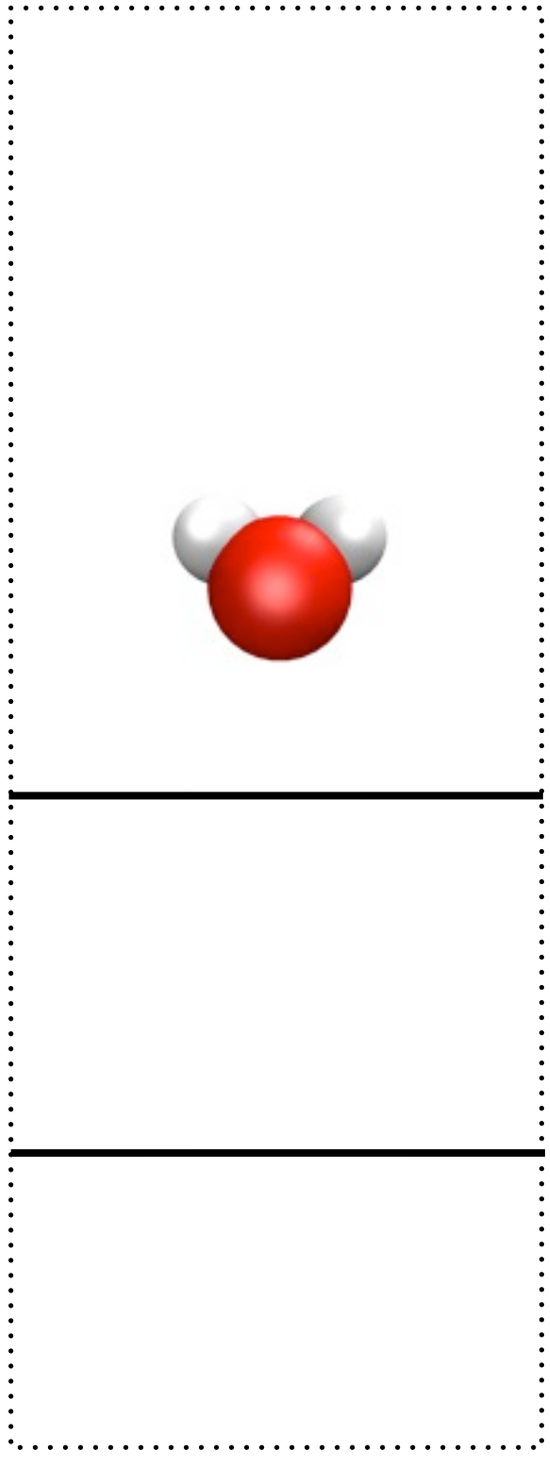


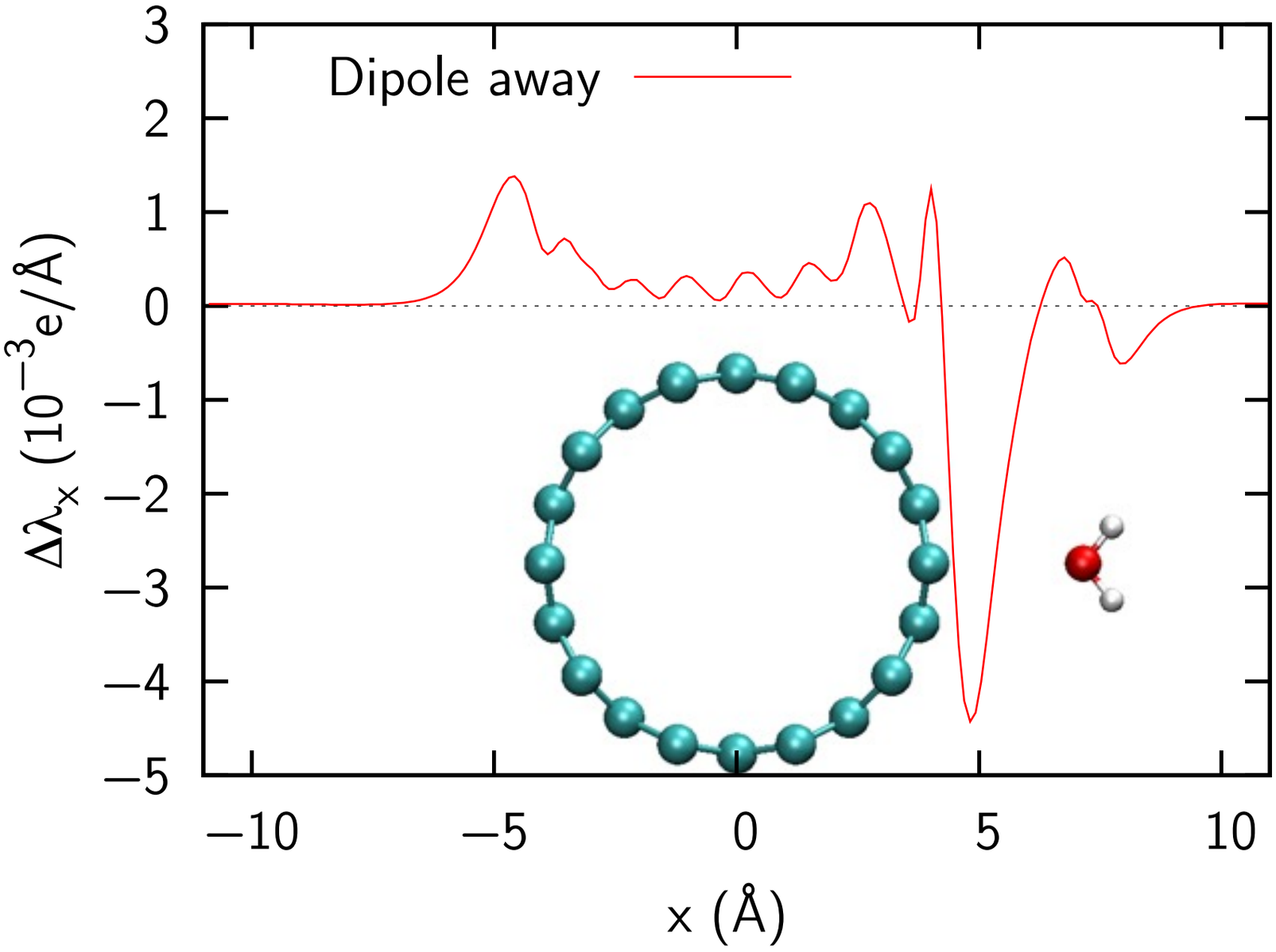

0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
−1.2
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT
model

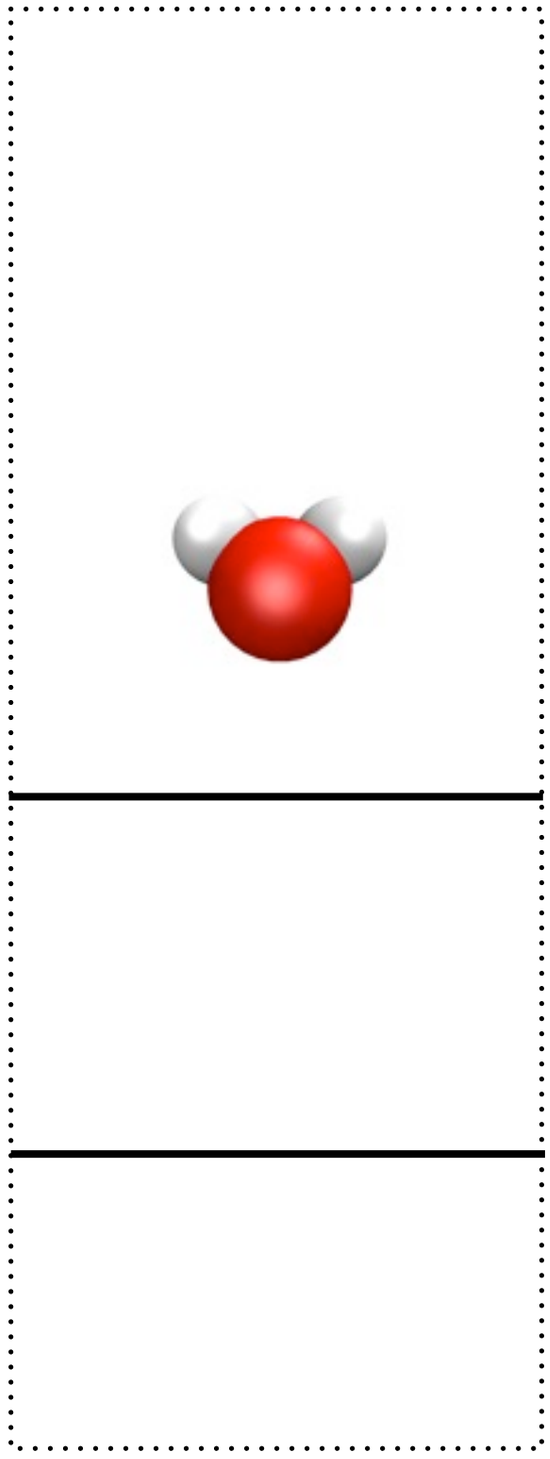

0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
−1.2
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT
model

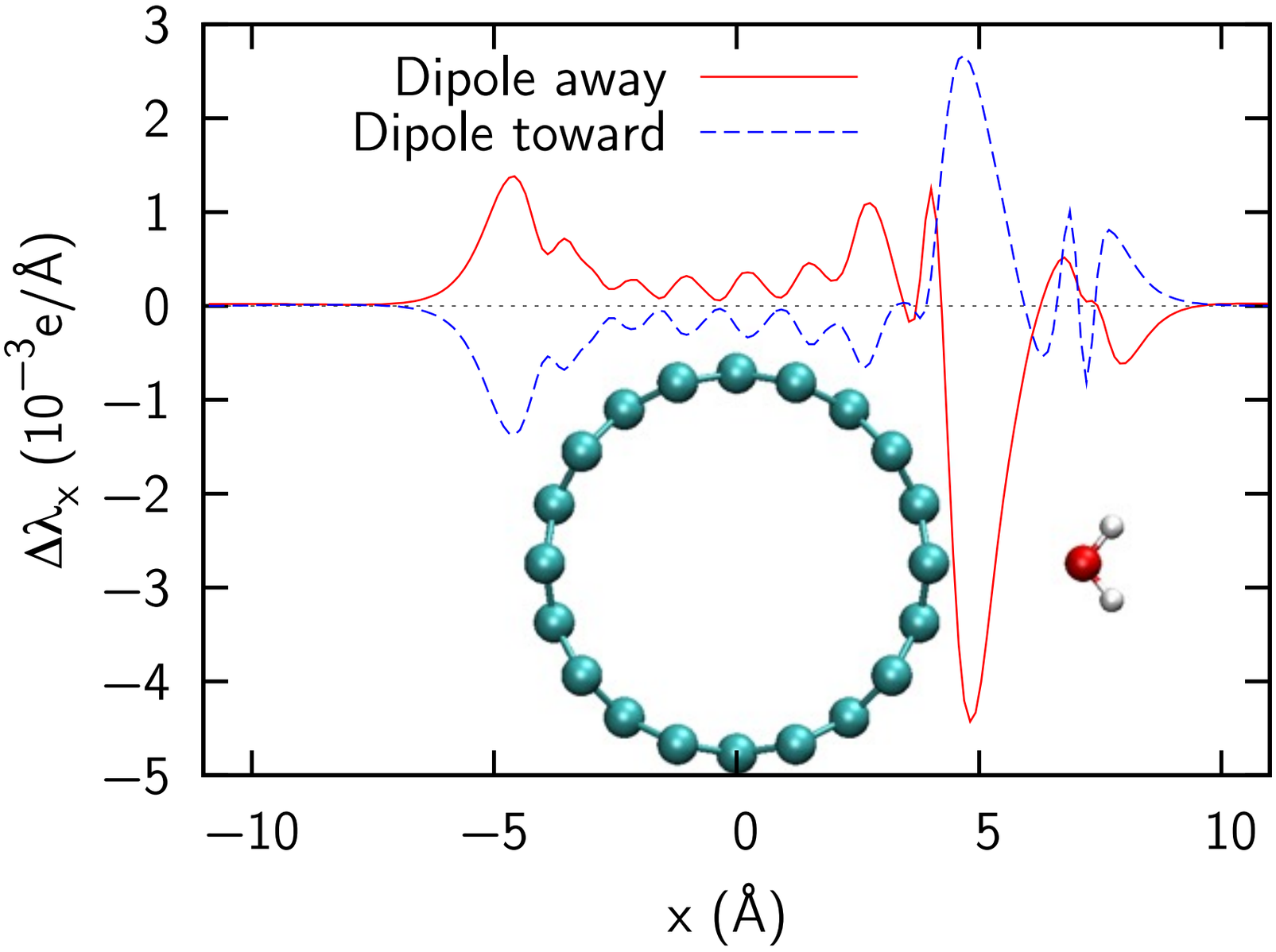

1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT
model


1.4
1.2
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
Δλ (10−3e/Å)
0
10
20
30
40
50
60
z (Å)
DFT
model



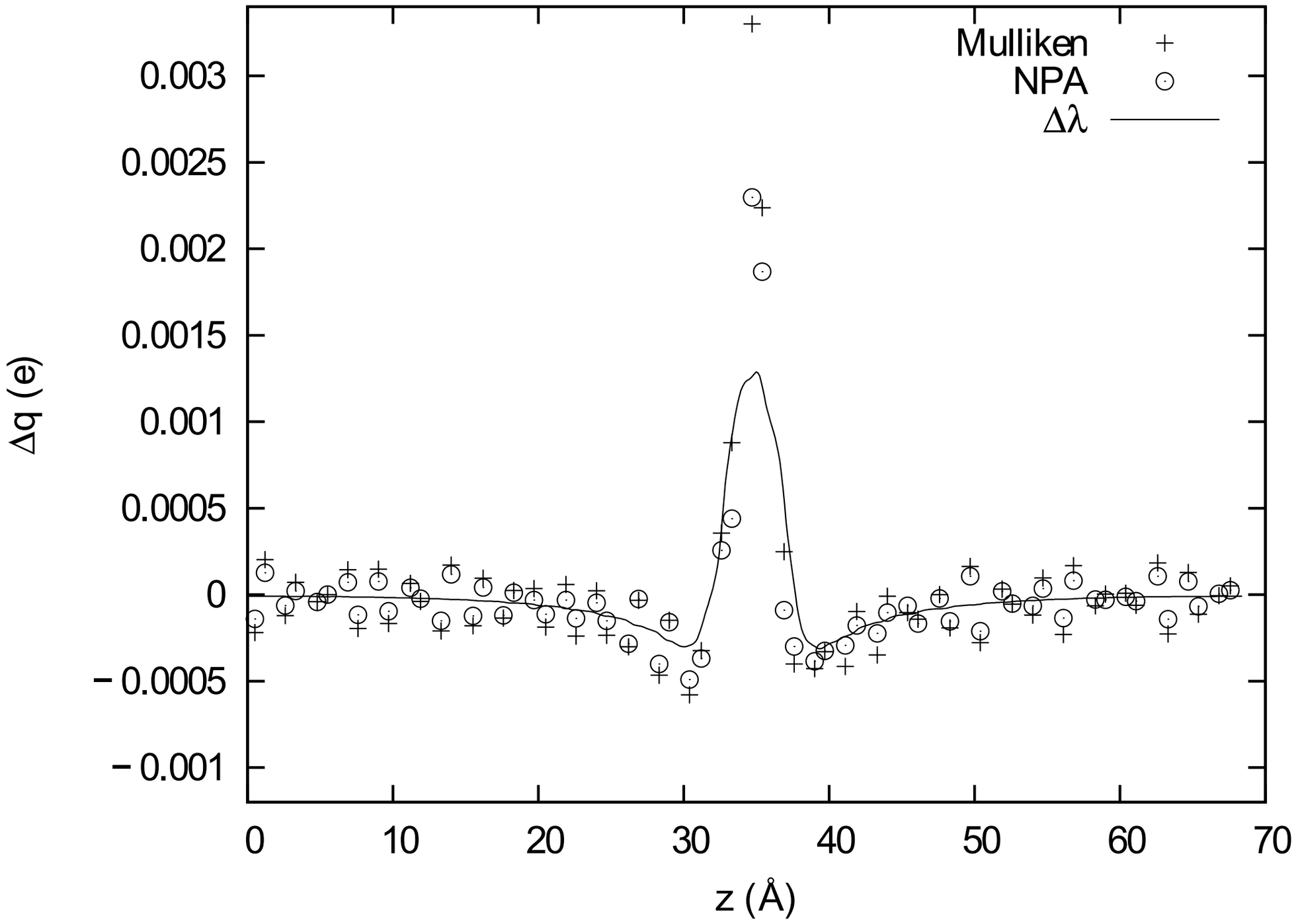

Dipole away
3
2
1
0
−1
−2
−3
−4
−5
−10
−5
0
5
10
x (Å)
$\Delta\lambda_x$ (10^{-3}e/Å)

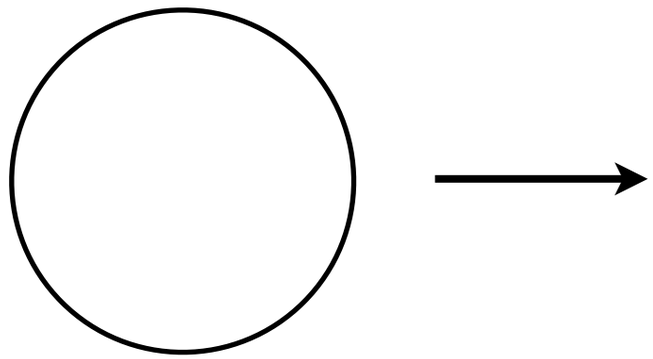


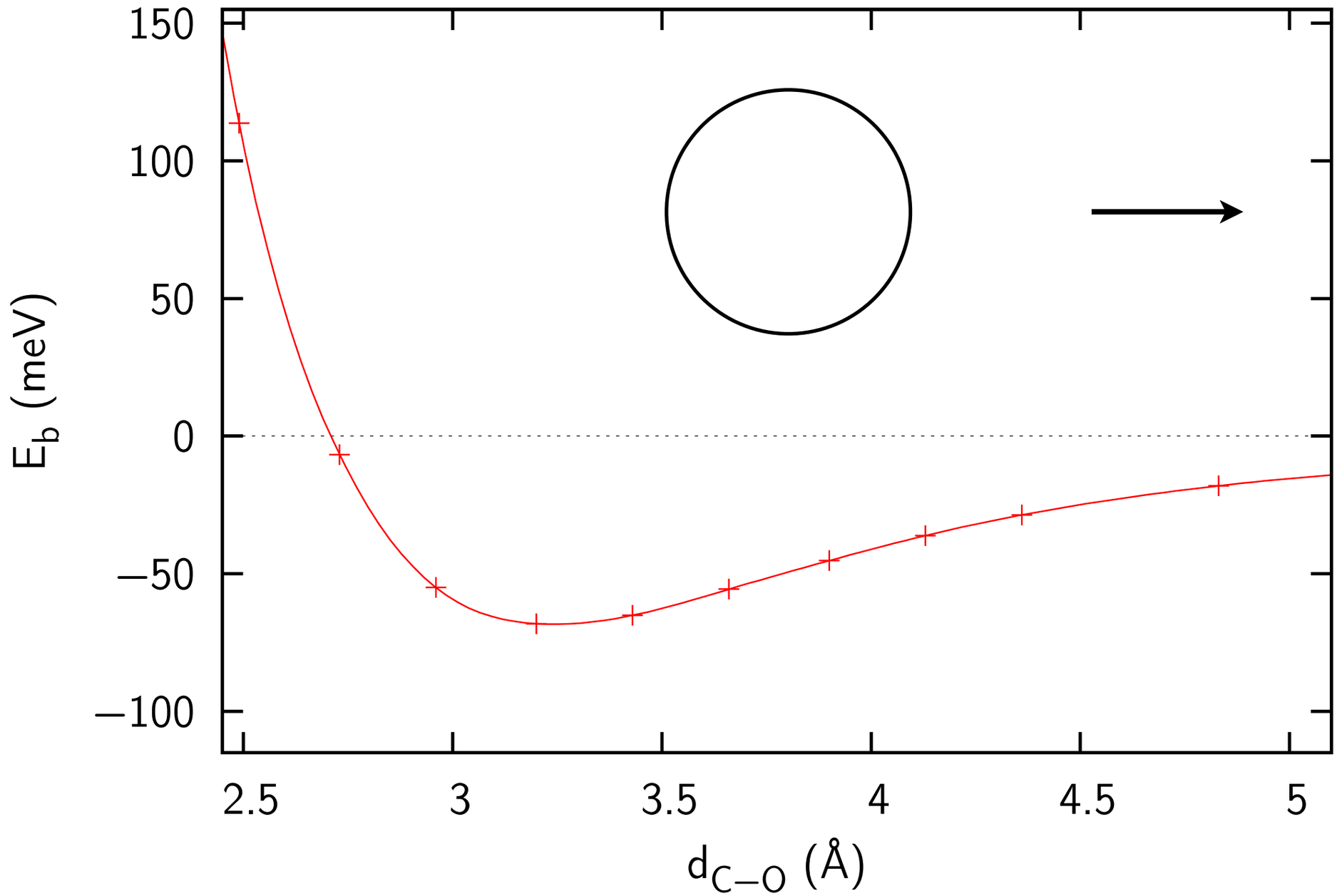

Dipole away
Dipole toward
3
2
1
0
−1
−2
−3
−4
−5
−10
−5
0
5
10
x (Å)
$\Delta\lambda_x$ (10^{-3}e/Å)

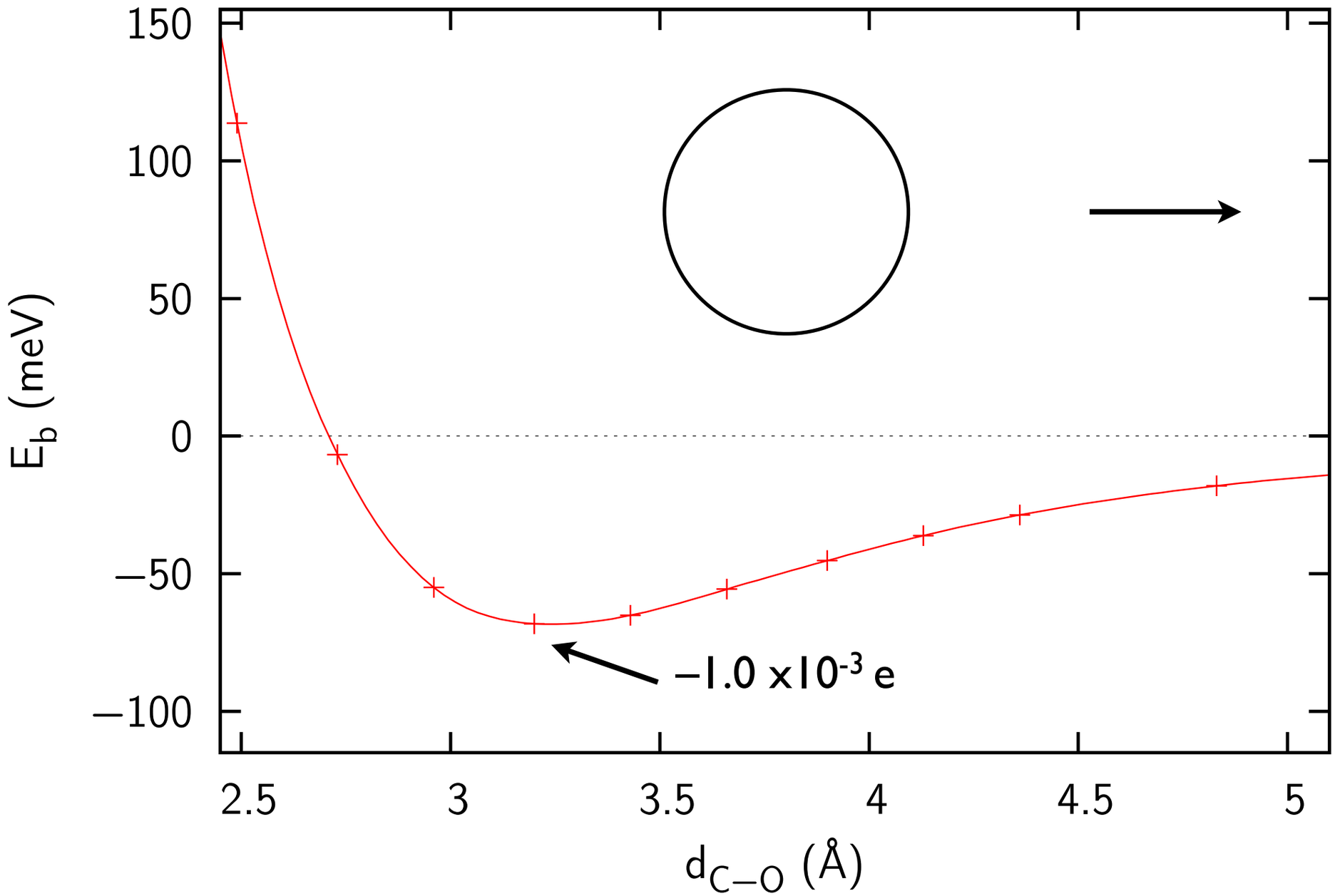
Summary

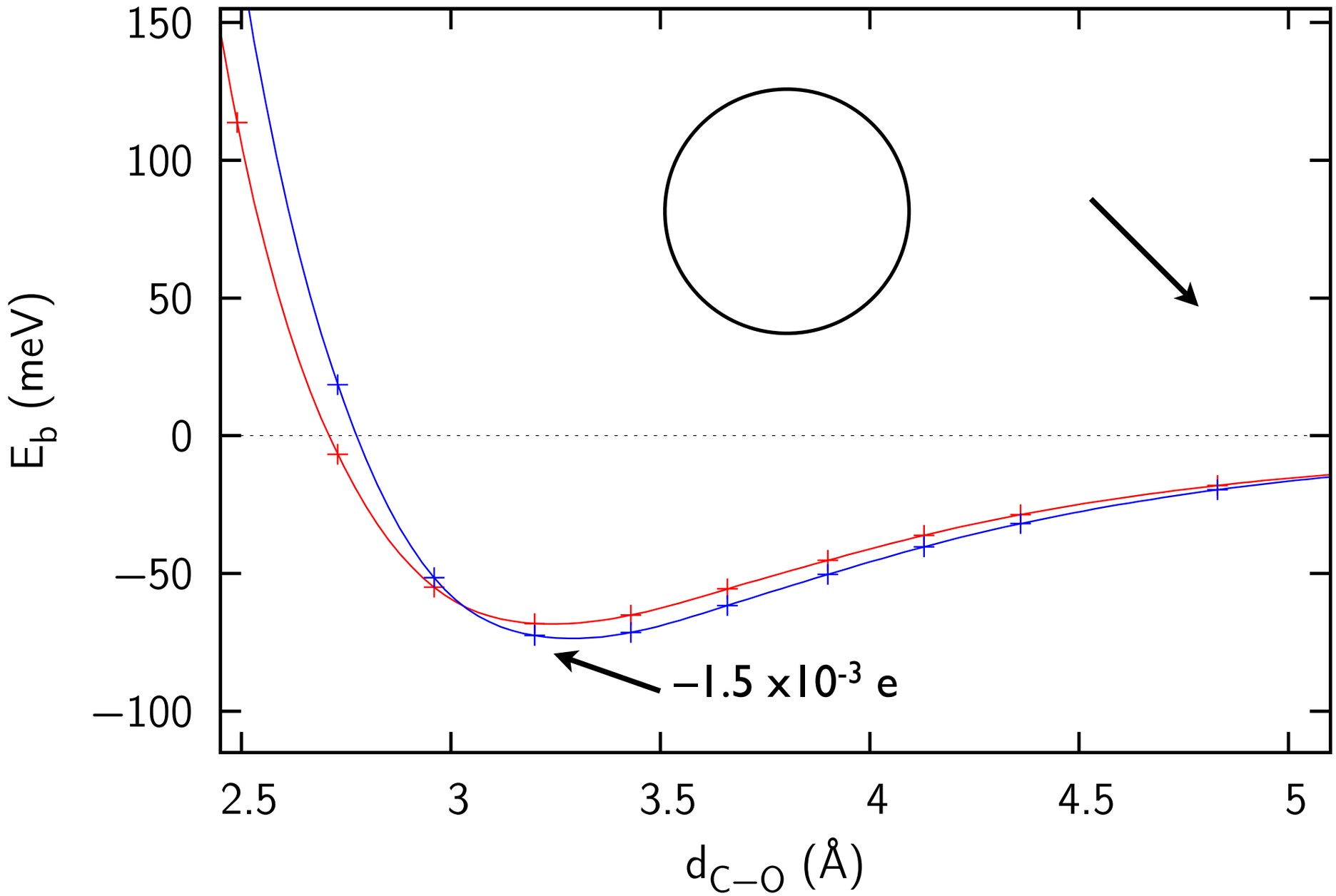
- Mulliken analysis has been consistently misinterpreted in the literature
- Electrostatic effects may be isolated through the use of classical charges
- There exists no charge transfer between water and CNTs

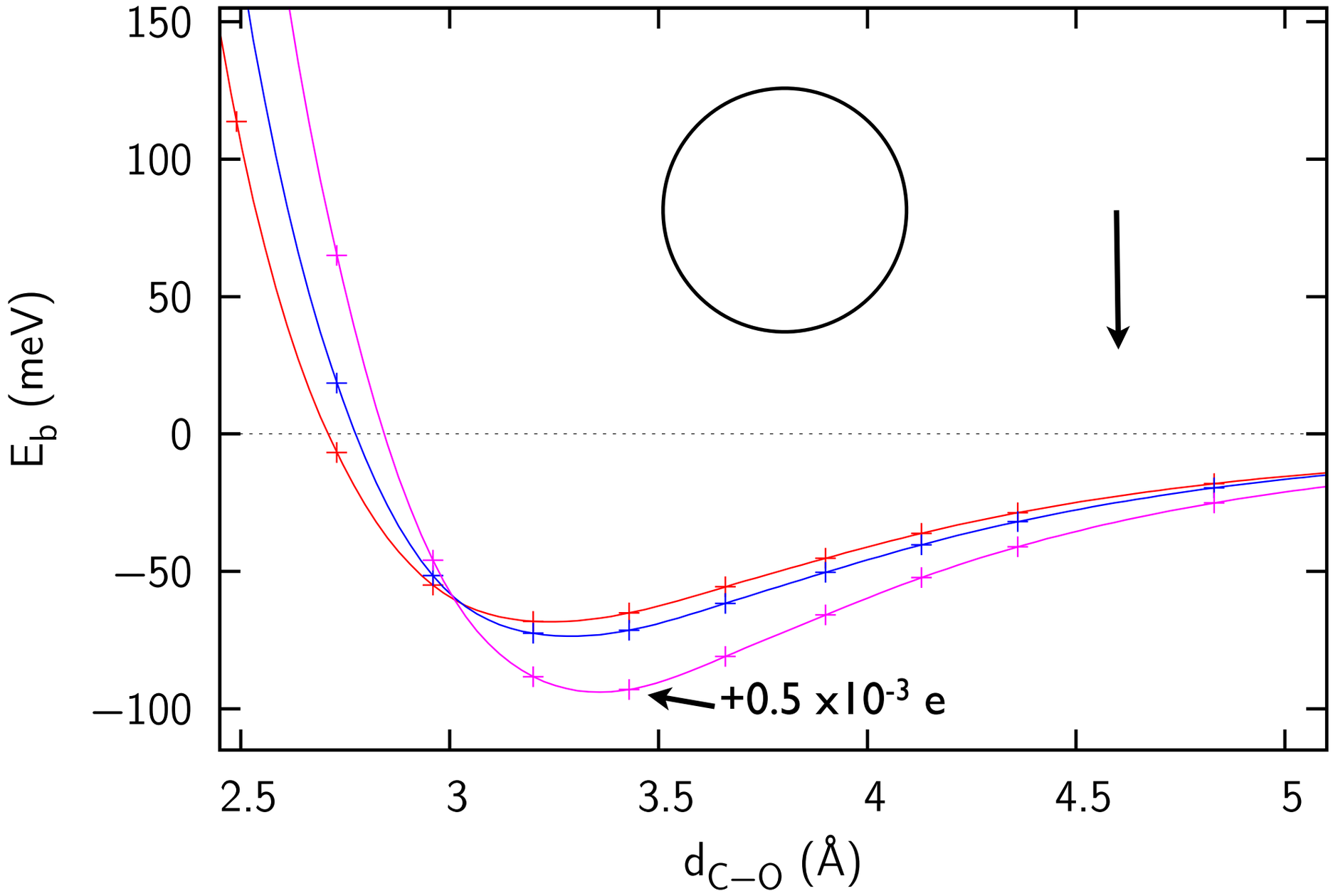

Mulliken
NPA
Δλ
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
− 0.0005
− 0.001
Δq (e)
0
10
20
30
40
50
60
70
z (Å)

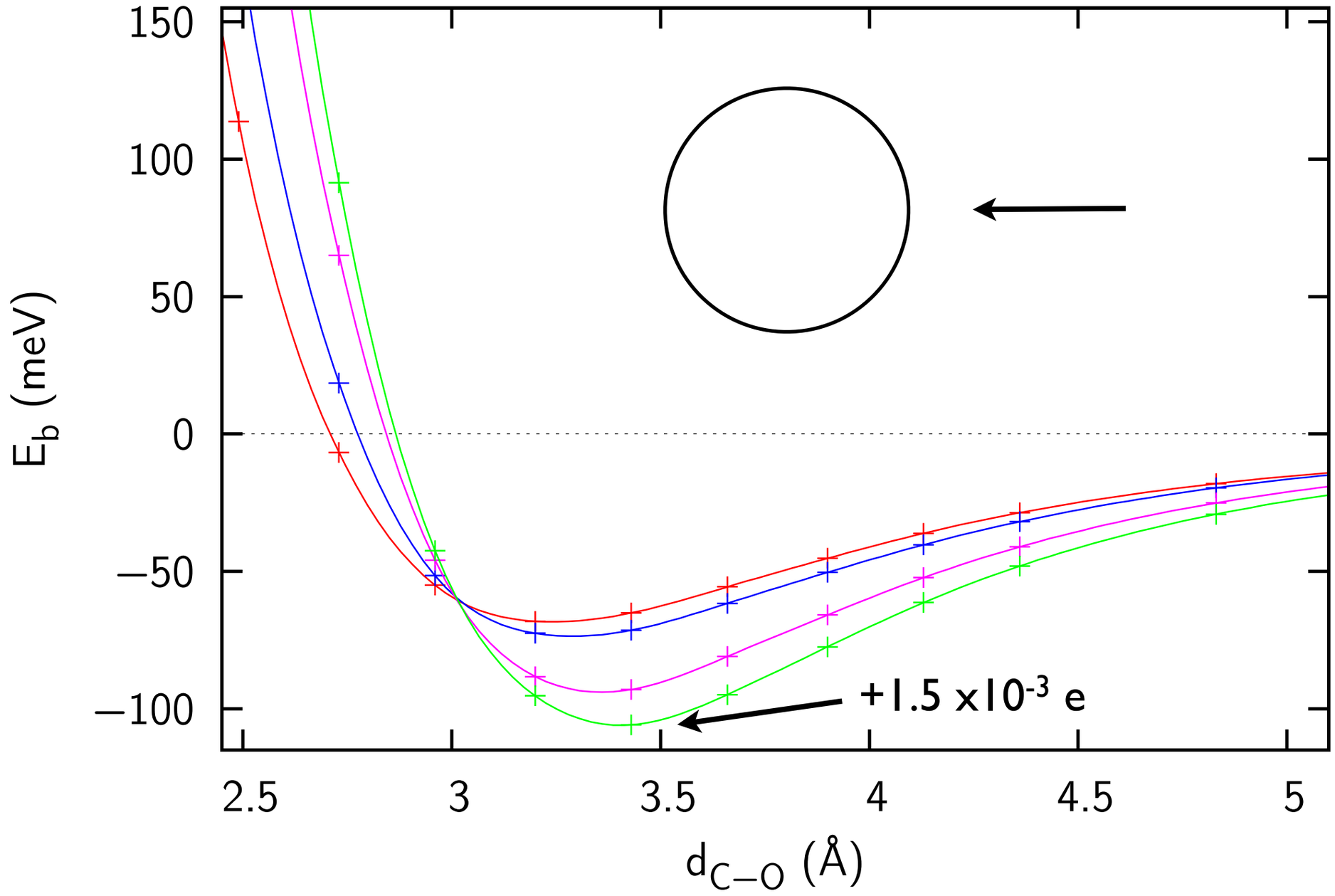


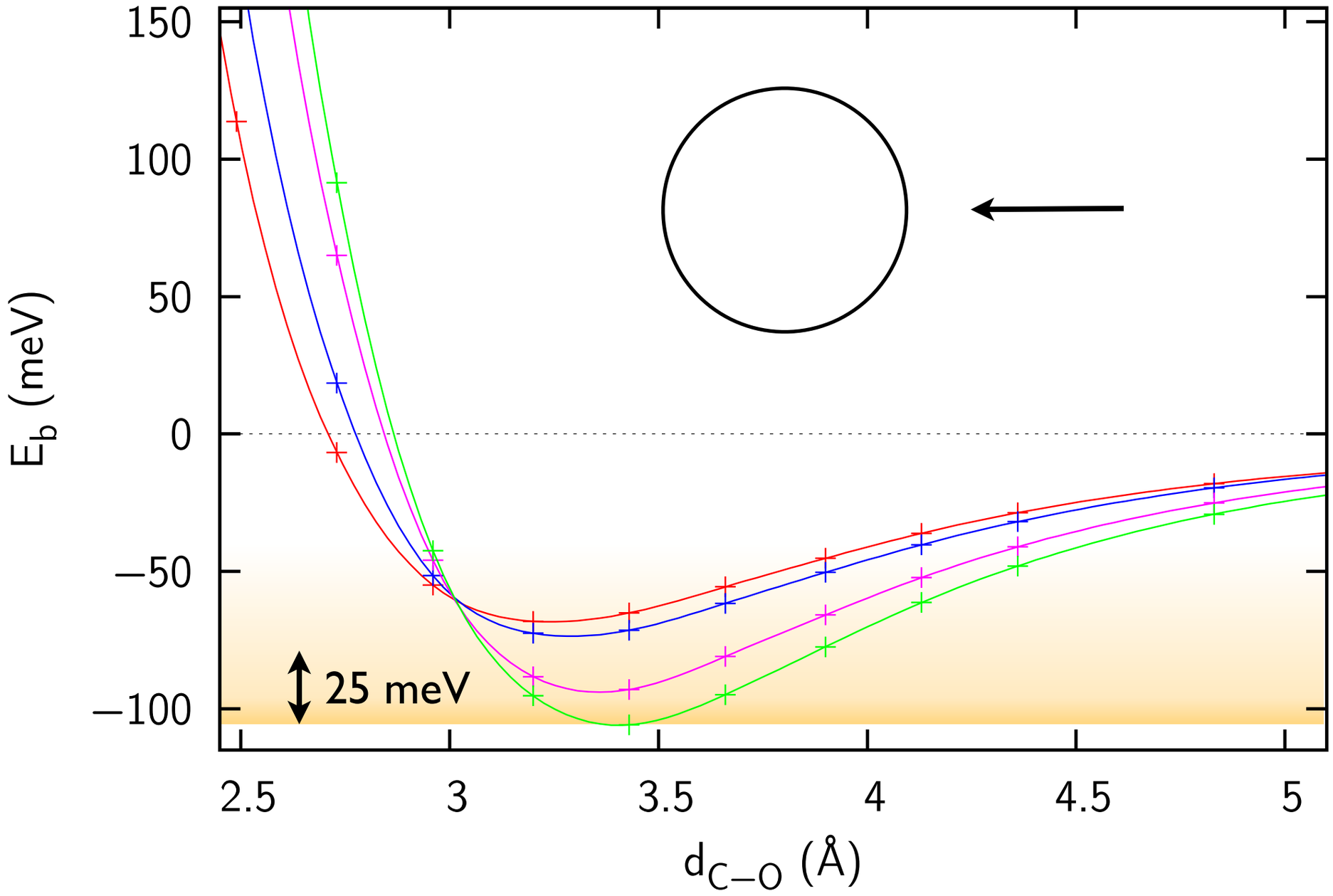

150
100
50
0
−50
−100
2.5
3
3.5
4
4.5
5
E_b (meV)
d_{C-O} (Å)

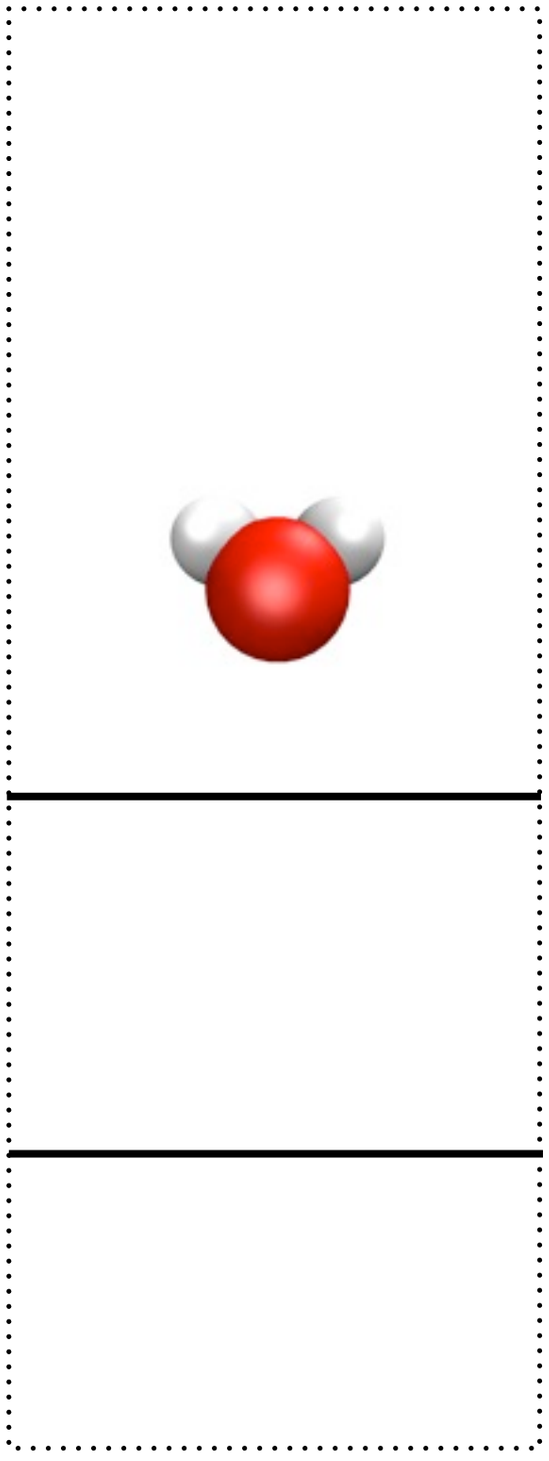

150
100
50
0
−50
−100
2.5
3
3.5
4
4.5
5
E_b (meV)
d_{C-O} (Å)
−1.0 x10^{-3} e


150
100
50
0
−50
−100
2.5
3
3.5
4
4.5
5
E_b (meV)
d_{C-O} (Å)
−1.5 x10^{-3} e


150
100
50
0
−50
−100
2.5
3
3.5
4
4.5
5
E_b (meV)
d_C−O (Å)
+0.5 x10^-3 e


150
100
50
0
−50
−100
2.5
3
3.5
4
4.5
5
E_b (meV)
d_C−O (Å)
+1.5 x10^-3 e


150
100
50
0
−50
−100
E_b (meV)
25 meV
2.5
3
3.5
4
4.5
5
d_{C-O} (Å)



Wednesday, 13 February 13

4.3 Angstrom

4.3 Angstrom

4.3 Angstrom

4.3 Angstrom

~ 40 meV





Wednesday, 13 February 13