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Structure and Dynamics of Hydrogen-Bonded Systems

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Quantization of Vibrations in H-Bonded Crystals

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Quantization of vibrations in H-bonded crystals

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ICTP meeting on the

Structure and Dynamics of Hydrogen-bonded systems

Trieste, 26-27 October 2009

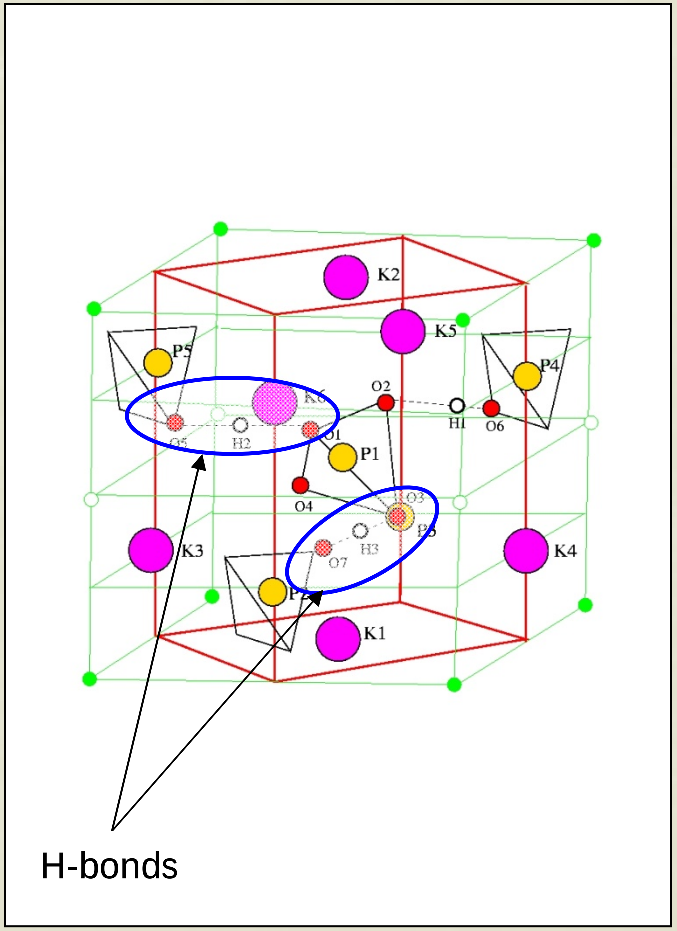
Outline

- Motivation: isotope effects in H-bonded crystals
- Lattice parameters and internal geometry of solids
    - Classical approach
    - Quasiharmonic approximation (QHA)
    - Exact solution and other approximations
- Applications
    - Model monoatomic and H-bonded chains
    - DFT H-bonded F-H…F linear chain
- Quality of DFT approximations
- Conclusions and Outlook

Isotope effects in the structure of solids: KDP vs DKDP

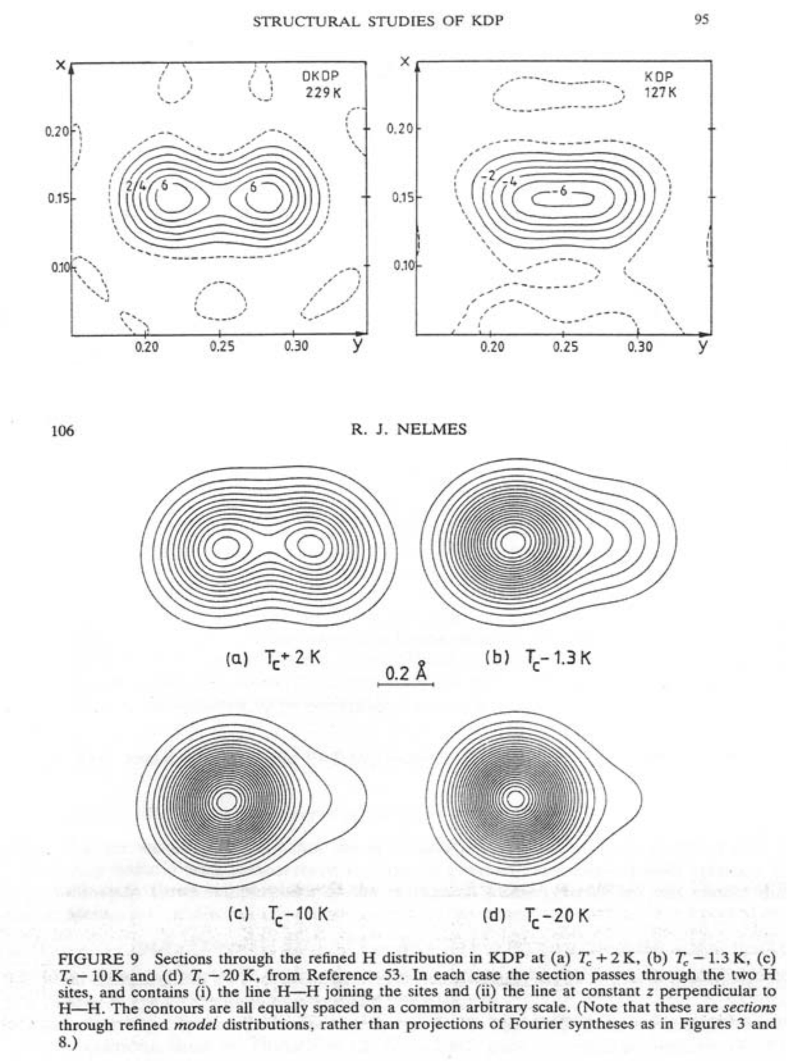
- **Huge isotope effect in ferroelectric T_c**: T_{KDP}=123 K vs T_{DKDP}=230 K (Isherwood and James, 1972)
- **Structural modifications (Ubbelohde effect)**: O-O distances (Ichikawa 1978) and lattice constants (Nelmes, Tun and Kuhs 1987)
- **Large family of H-bonded molecular crystals**, including ferro and antiferroelectric materials (**ADP, Squaric acid, LHP, ice,** …)
- **Organic crystals,** polymorphism is very important for **Pharmaceutical industry**

Distributions reconstructed from elastic neutron scattering do not show the potential minima



Neutron scattering

[Nelmes, Ferroelectrics **71**, 87 (1987)]



STRUCTURAL STUDIES OF KDP 95

106 R. J. NELMES

FIGURE 9 Sections through the refined H distribution in KDP at (a) $T_c + 2$ K, (b) $T_c - 1.3$ K, (c) $T_c - 10$ K and (d) $T_c - 20$ K, from Reference 53. In each case the section passes through the two H sites, and contains (i) the line H—H joining the sites and (ii) the line at constant *z* perpendicular to H—H. The contours are all equally spaced on a common arbitrary scale. (Note that these are *sections* through refined *model* distributions, rather than projections of Fourier syntheses as in Figures 3 and 8.)

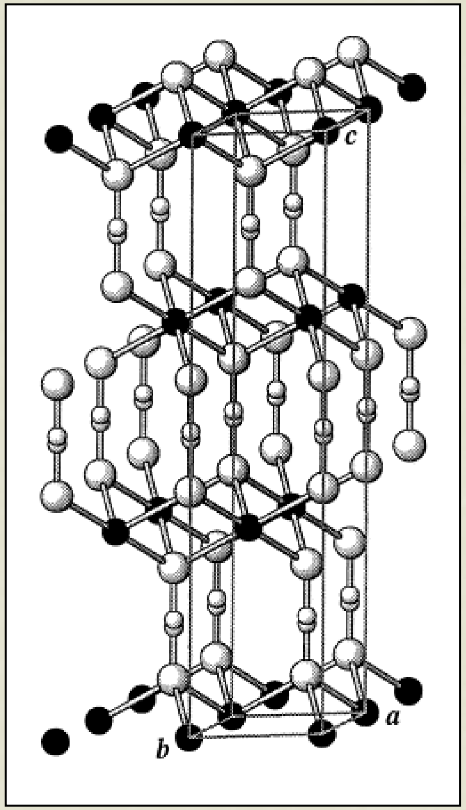
CrOOH(D): Structure and thermodynamics

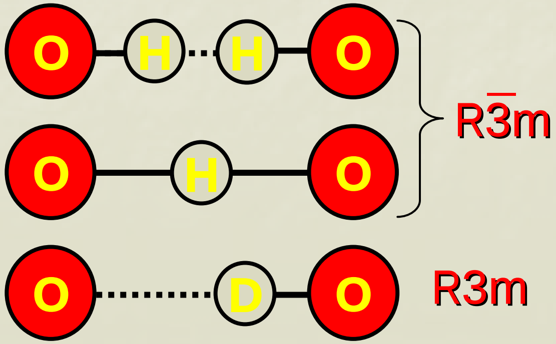
(Keith Refson, next talk)

Structural modifications upon deuteration

[Christensen, Hansen and Lehmann, J. Solid State Chem. 21, 325 (1977)]

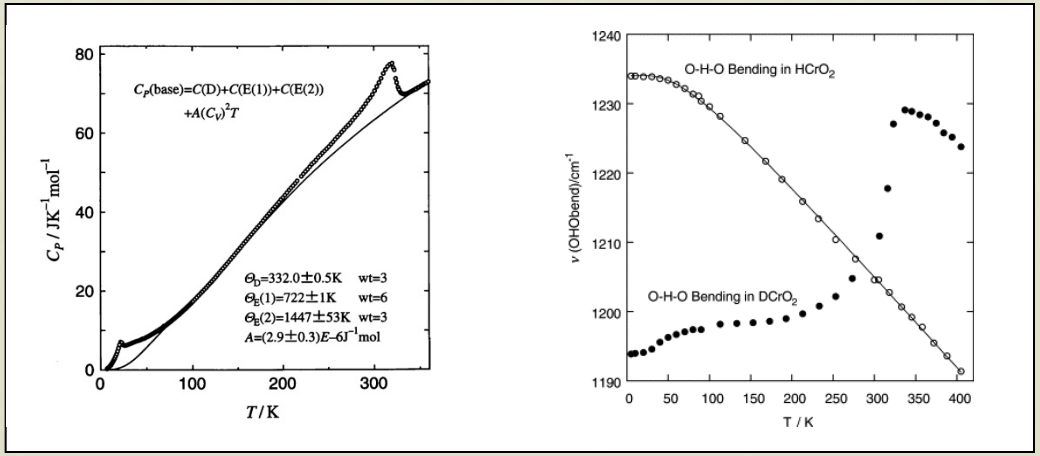
	CrOOH	CrOOD
Space Group	$R\bar{3}m$ (csym)	$R3m$
c (Å)	13.37	13.48
a (Å)	2.979	2.985
d[O-O] (Å)	2.47	2.57





Phase transition in CrOOD at 320K

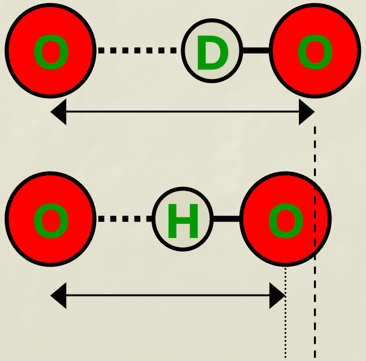
[Matsuo et al., J. Mol. Struc. **790**, 129 (2006)]



Questions

1. What is the origin of quantum (isotope) effects in d[O-O] and lattice parameters?
    - Tunneling or geometric effect?
2. When are these important?
3. Can we deal with this in an inexpensive, efficient way?
4. What level of approximation is acceptable?

The Ubbelohde effect



Structural and dynamical properties of crystals: classical approach

- Born-Oppenheimer approximation for electrons (*E*)
- Classical equilibrium configuration (minimize *E*), or classical lattice parameters and equilibrium configuration (minimize $H=E+\sigma.\tau$)
- Force constants and dynamical matrix (second derivatives of the potential @ classical equilibrium structure)
- Phonon dispersion relations and vibrational normal modes.

Problem

Quantization of vibrations (Zero-point-motion - ZPM) not taken into account.

1. Lattice parameters (e.g. volume) are incorrect (ZP pressure shifts equilibrium)
2. Internal geometry can also be incorrect.
3. Mechanical and thermodynamic properties, e.g. phase transitions.

Introducing zero-point-motion

- Express Hamiltonian in terms of {Q_i}, a set of orthogonal vibrational coordinates: $\mathbf{Q} = \mathbf{A}^{-1}\mathbf{q}$, with **q**=mass-scaled coordinates:

$$\boxed{H(Q_1,\cdots,Q_{3N}) = -\frac{\hbar^2}{2}\sum_{i=1}^{3N}\frac{d^2}{dQ_i^2} + V_{tot}(Q_1,\cdots,Q_{3N})}$$

- **Harmonic approximation**: expand potential to 2nd order in {Q_i} around a stationary point :

$$\boxed{V_{tot}(Q_1,\cdots,Q_N) \approx E_0 + \frac{1}{2}\sum_{i=1}^{3N}\omega_i^2 Q_i^2}$$

$$\boxed{E_{HA} = E_0 + \frac{\hbar}{2}\sum_{i=1}^{3N}\omega_i}$$

Within HA,
<Q_i>=0

Internal geometry
not modified

- **Periodic solids**: Brillouin zone averaging

$$\boxed{E_{HA} = E_0 + \frac{\hbar}{2}\sum_{i=1}^{3M}\int g(\mathbf{k})\,\omega_i(\mathbf{k})\,d\mathbf{k}}$$

$g(\mathbf{k})$ = phonon density of states

Quasi-harmonic approximation (QHA)

- Quasi-harmonic approximation (QHA): frequencies depend on lattice parameters.
- Free energy: includes quantum and thermal effects.

$$\boxed{F_{QHA}(V) = E_0(V) + \frac{\hbar}{2}\sum_{i=1}^{3M}\int g(\mathbf{k})\,\omega_i(\mathbf{k},V)\,d\mathbf{k} + k_B T\sum_{i=1}^{3M}\int g(\mathbf{k})\ln\left[1-\exp\left(-\frac{\hbar\omega_i(\mathbf{k},V)}{k_B T}\right)\right]d\mathbf{k}}$$

- Minimization with respect to V gives finite-temperature, quantum-corrected equilibrium volume and internal geometry.

Limitations of the QHA

- Vibrations still treated as a collection of non-interacting harmonic oscillators.
- Anharmonicity only through V-dependence of ZPE.
- Excluded in QHA:
  - Intra-mode anharmonicity: higher orders in the same mode (e.g. Q^4)
  - Mode coupling: products of modes (e.g. $Q_i^2 Q_j$)

The other extreme: exact solution

1. Express Hamiltonian in terms of $\{Q_i\}$, a set of orthogonal vibrational coordinates: $\mathbf{Q} = \mathbf{A}^{-1}\mathbf{q}$. Rigid translations eliminated. No rigid rotations.

2. Map potential energy surface (PES): $\boxed{V(Q_1, \cdots, Q_{3N-3})}$

3. Solve (*3N-3*)-dimensional vibrational Schrödinger equation:

$$\boxed{\left[-\frac{\hbar^2}{2}\sum_i \frac{d^2}{dQ_i^2} + V(Q_1,\cdots,Q_{3N-3})\right]\Psi(Q_1,\cdots,Q_{3N-3}) = E\,\Psi(Q_1,\cdots,Q_{3N-3})}$$

4. Calculate mean values of vibrational coordinates:

$$\boxed{\langle Q_i \rangle = \int\cdots\int Q_i \left|\Psi(Q_1,\cdots,Q_{3N-3})\right|^2 dQ_1\cdots dQ_{3N-3}}$$

5. Obtain quantum-averaged internal geometry via: $\boxed{\langle \mathbf{q} \rangle = \mathbf{A}\langle \mathbf{Q} \rangle}$

Approximations: VSCF

[For molecules: Ratner and Gerber, J. Phys. Chem. **90**, 20 (1986)]

1. Vibrational self-consistent field (VSCF/Hartree): Approximate total wave function as product of single-mode wave functions. Modes uncorrelated.

$$\boxed{\Psi_{VSCF}(Q_1,\cdots,Q_{3N-3}) = \prod_{i=1}^{3N-3}\phi_i(Q_i)}$$

2. Solve a set of *(3N-3)* coupled one-dimensional Schrödinger equations:

$$\left[-\frac{\hbar^2}{2}\frac{d^2}{dQ_i^2}+V_i^{VSCF}(Q_i)\right]\phi_i(Q_i)=\varepsilon_i\,\phi_i(Q_i)$$

3. With:

$$\boxed{V_i^{VSCF}(Q_i)=\int\cdots\int V(Q_1,\cdots,Q_{3N-3})\prod_{j\neq i}\left|\phi_j(Q_j)\right|^2 dQ_j}$$

4. And energy:

$$E_{VSCF}=\sum_{i=1}^{3N-3}\varepsilon_i-(3N-7)\underbrace{\int V_1(Q_1)\left|\phi_1(Q_1)\right|^2 dQ_1}_{\boxed{\text{Double counting}}}$$

Mean values:

$$\boxed{\langle Q_i\rangle=\int Q_i\left|\phi_i(Q_i)\right|^2 dQ_i}$$

Internal geometry can change in VSCF

Further approximations

1. Anharmonic: Approximate wave function as product of single-mode wfn:

$$\Psi_{VSCF}(Q_1,\cdots,Q_{3N-3}) = \prod_{i=1}^{3N-3} \phi_i(Q_i)$$

2. And the single-mode potentials as:

$$\boxed{V_i^{ANH}(Q_i) = V(0,\cdots,Q_i,\cdots,0)}$$

3. Solve the *(3N-3)* uncoupled one-dimensional Schrödinger equations:

$$\left[-\frac{\hbar^2}{2}\frac{d^2}{dQ_i^2} + V_i^{ANH}(Q_i)\right]\phi_i(Q_i) = \varepsilon_i\,\phi_i(Q_i)$$

4. with energy given by: $E_{ANH} = \sum_{i=1}^{3N-3}\varepsilon_i$

Mean values:

$$\boxed{\langle Q_i\rangle = \int Q_i |\phi_i(Q_i)|^2\, dQ_i}$$

Internal geometry can change in ANH and ZO

5. Zero-order: $\boxed{V_i^{ZO}(Q_i) = V(\langle Q_1\rangle,\cdots,Q_i,\cdots,\langle Q_{3N-3}\rangle)}$ is like VSCF but …

single-mode wave functions ≈ δ-functions centered at the mean values.

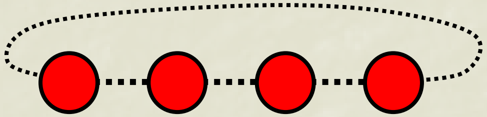
Summary of Methods

1. Quasi-harmonic approximation (QHA): €
   - a. Recovers anharmonic effects mediated by volume changes.
   - b. Ignores intra-mode and mode-coupling anharmonicity
2. Anharmonic approximation (ANH): €€ Zero-order (ZO): €€
   - a. Recovers intra-mode anharmonicity. Recovers some mode-coupling anh.
   - b. Ignores mode-coupling anharmonicity. Double-well potentials tricky.
3. Vibrational self-consistent field (VSCF): €€€
   - a. Recovers intra-mode anharmonicity.
   - b. Recovers mode-coupling anharmonicity in mean-field.
   - c. Ignores correlation between modes.
4. Partially correlated schemes [e.g. P+($3N$-3-P)]: €€€€
5. Exact: €€€€€ (unfeasible for more than 6 modes)

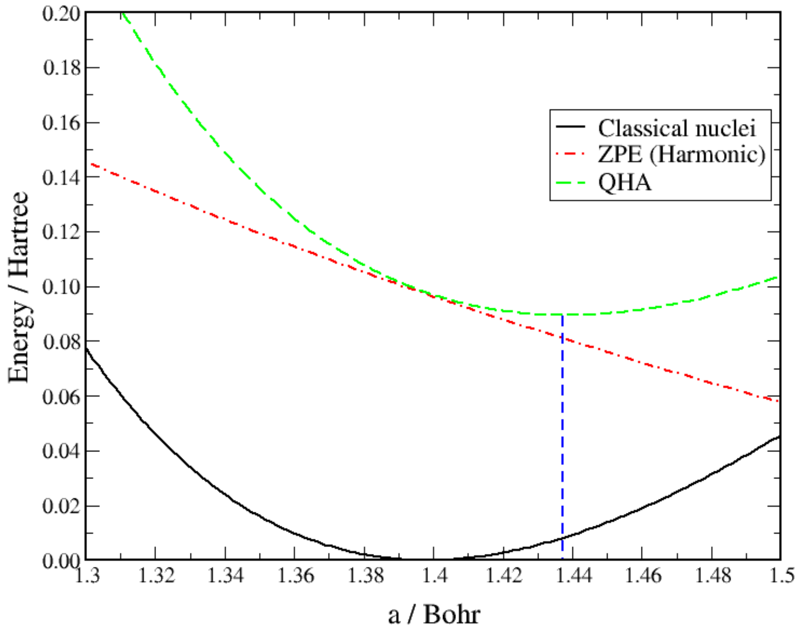
Monoatomic linear chain

I. Scivetti, N. Gidopoulos and J. Kohanoff, Phys. Rev. B **78**, 224108 (2008)

For a periodic linear chain:



$$E_{QHA}^{1D}(a) \approx E_0(a) + \frac{\hbar}{2}\sum_{n=1}^{N}\omega_n(a)$$

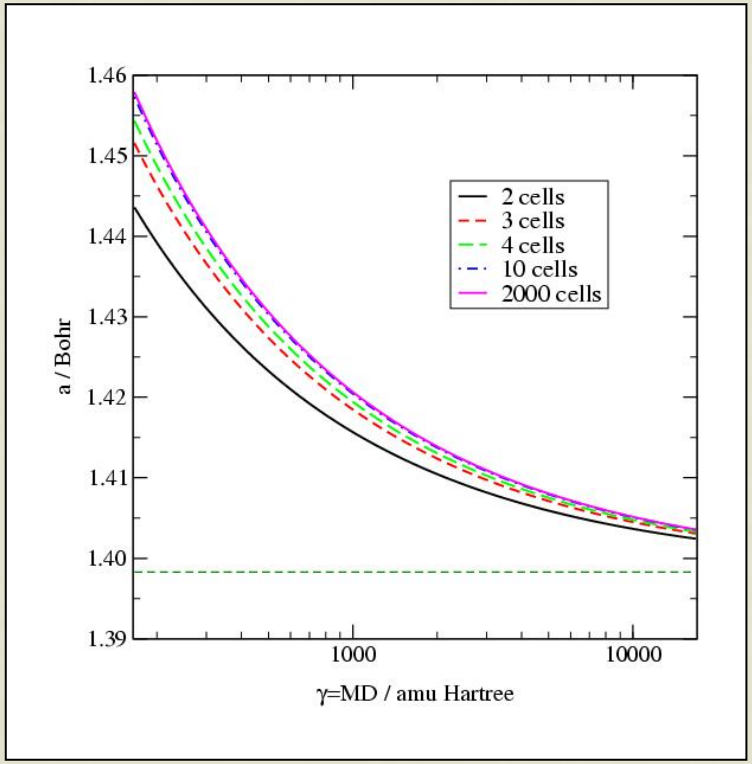


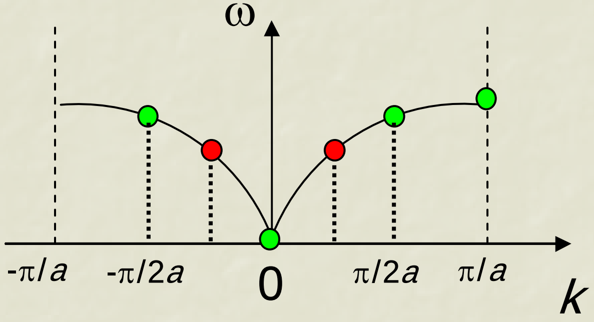
ω increases upon compression

Expansion due to quantum effects (ZPE)

Monoatomic anharmonic chain:
Brillouin zone sampling

Morse potential: $V(x) = D\left[1 - \exp\left(-b(x - x_0)\right)\right]^2$





Number of cells = number of k-points

The relevant quanticity parameter is: $\gamma = mD$ with m=mass of the particles

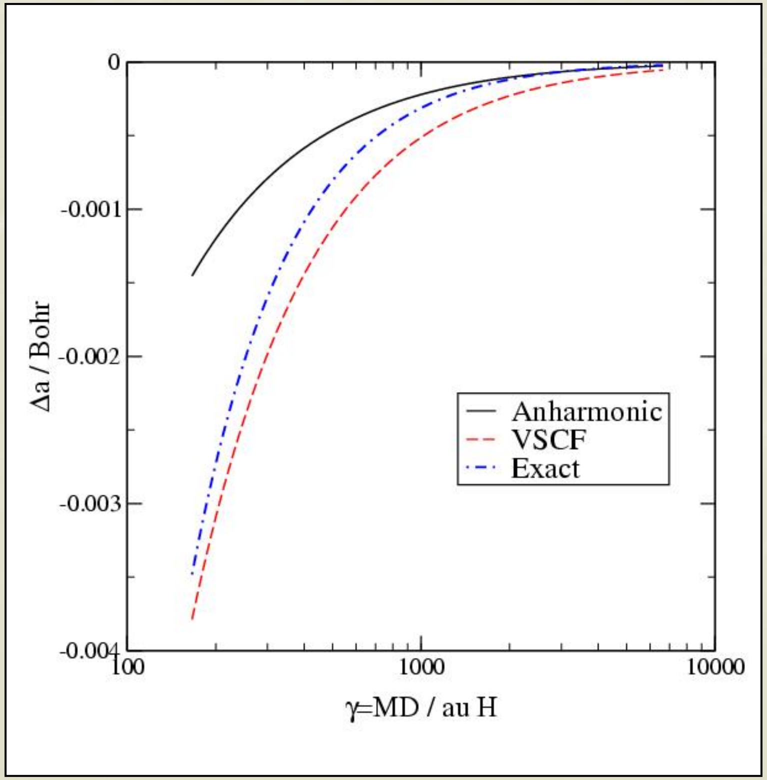
Within the QHA

- 10 k-points: *a* is fully converged
- 4 k-points: *a* is excellent
- 2 k-points, *a* is 1% too low at γ=135

Monoatomic anharmonic chain: comparison of approximations

Morse potential: $V(x) = D\left[1-\exp\left(-b(x-x_0)\right)\right]^2$

Differences with respect to the QHA



4 cells (3 vibrational d.o.f.)

Exact and VSCF: Solve Schrödinger using DVR in the form of Lagrange meshes

[Baye and Heenen, J. Phys. A **19**, 2041 (1986)]

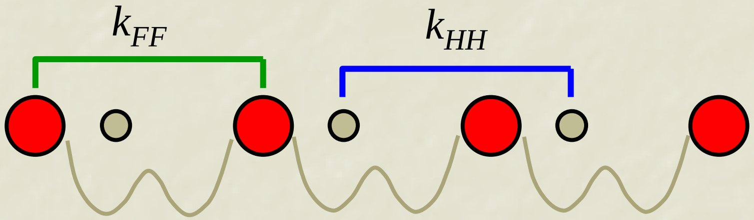
[Varga, Zhang and Pentelides, PRL **93**, 196403 (2004)]

- Anharmonic: 0.1% below QHA
- Exact: 0.3% below QHA
- VSCF: within 0.05% of exact value

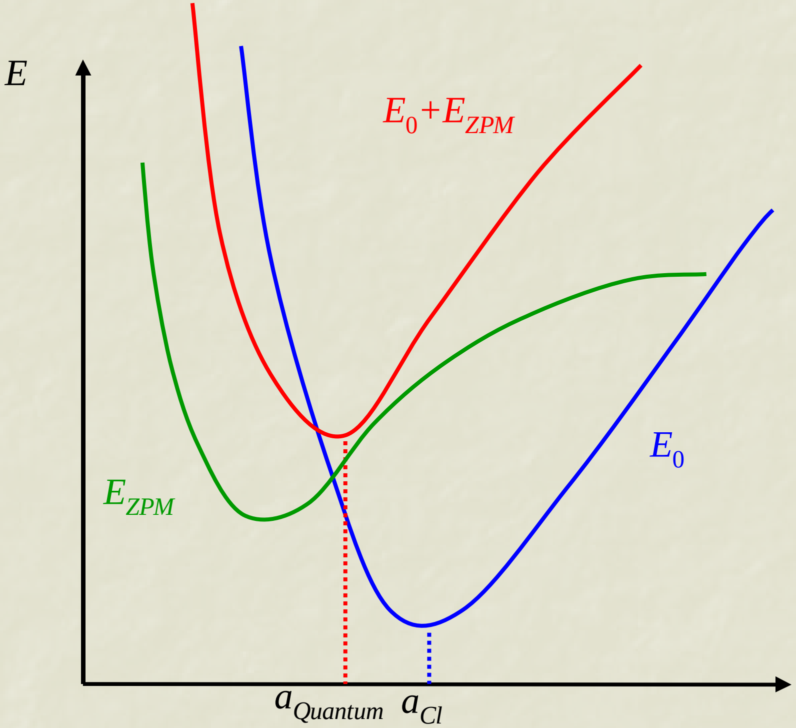
QHA lattice constant is extremely good

Model H-bonded chain

[Yanovitskii, Vlastou-Tsinganos and Flytzanis, PRB **48**, 12645 (1993)]



- H-atoms move in a double-well potential
- k_{HH} spring enforces ice rules.
- k_{FF} spring disfavors $[FHF]^-$
- Morse on F-F distance (dependence on a)



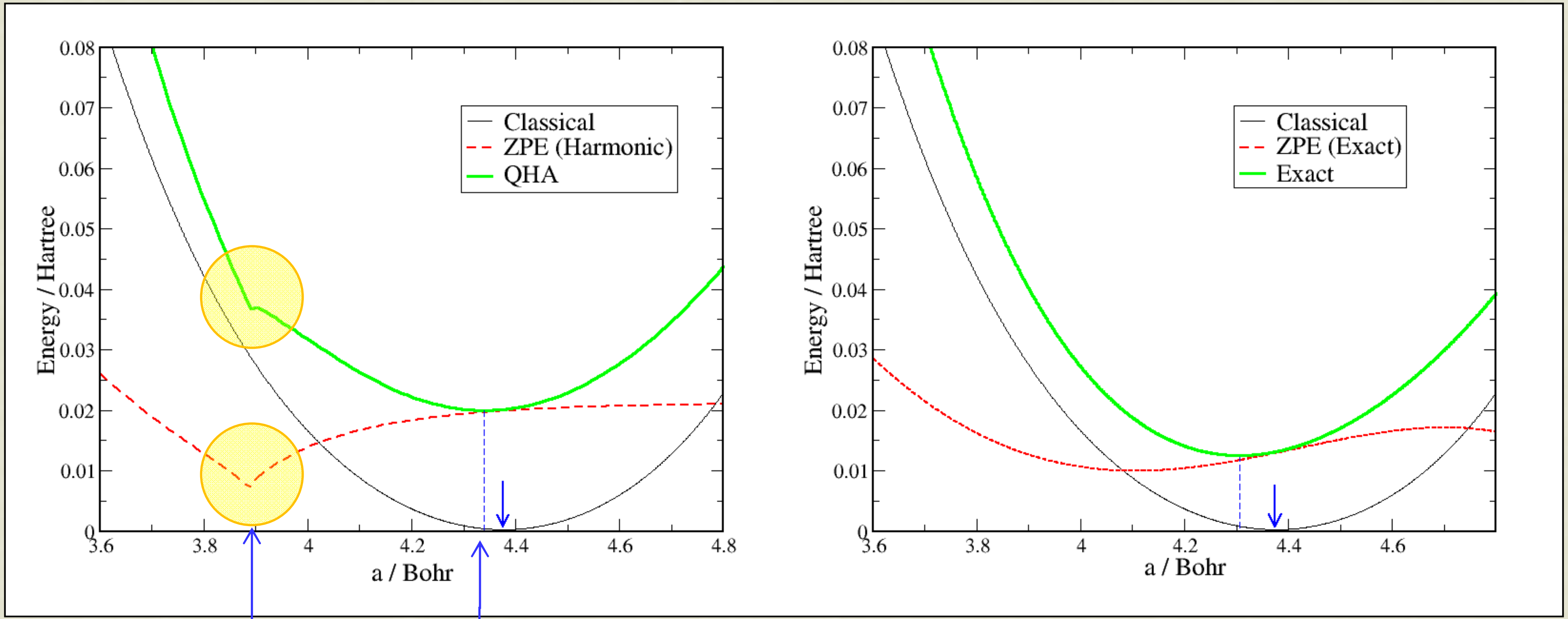
For H-bonds, ω decreases upon compression.

Therefore, the lattice constant reduces

Model H-bonded chain

QHA vs exact solution

I. Scivetti, N. Gidopoulos and J. Kohanoff, Phys. Rev. B **78**, 224108 (2008)

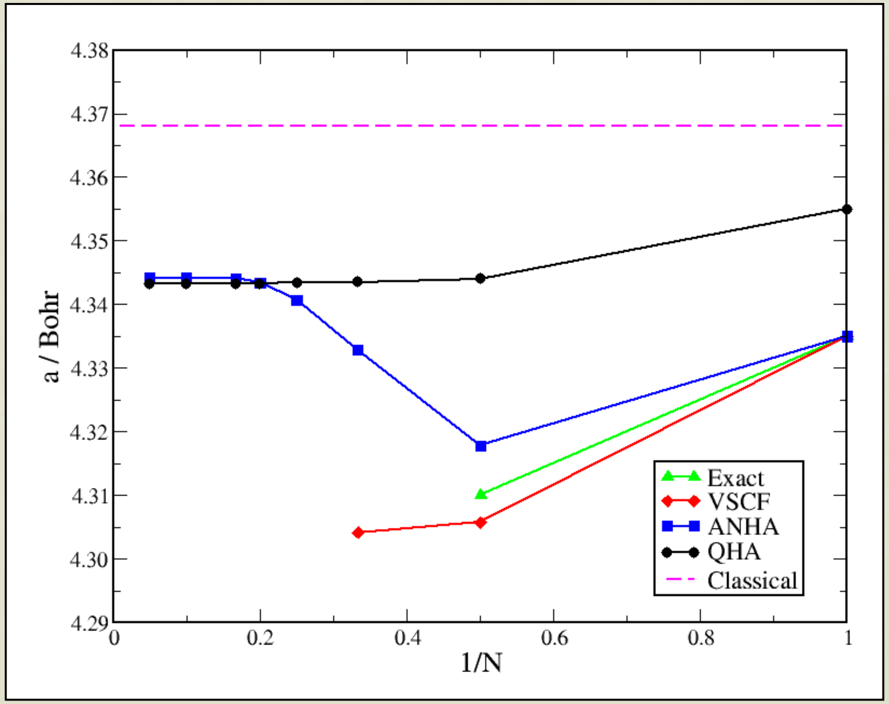


QHA underestimates the contraction

Secondary (spurious) minimum appears upon H centering

Model H-bonded chain: comparison of approximations

a_{Cl} = 4.368 Bohr



- QHA only from minimum (can't be done from saddle point)
- ANH using normal modes at minimum.
- ANH using saddle point modes is poor.

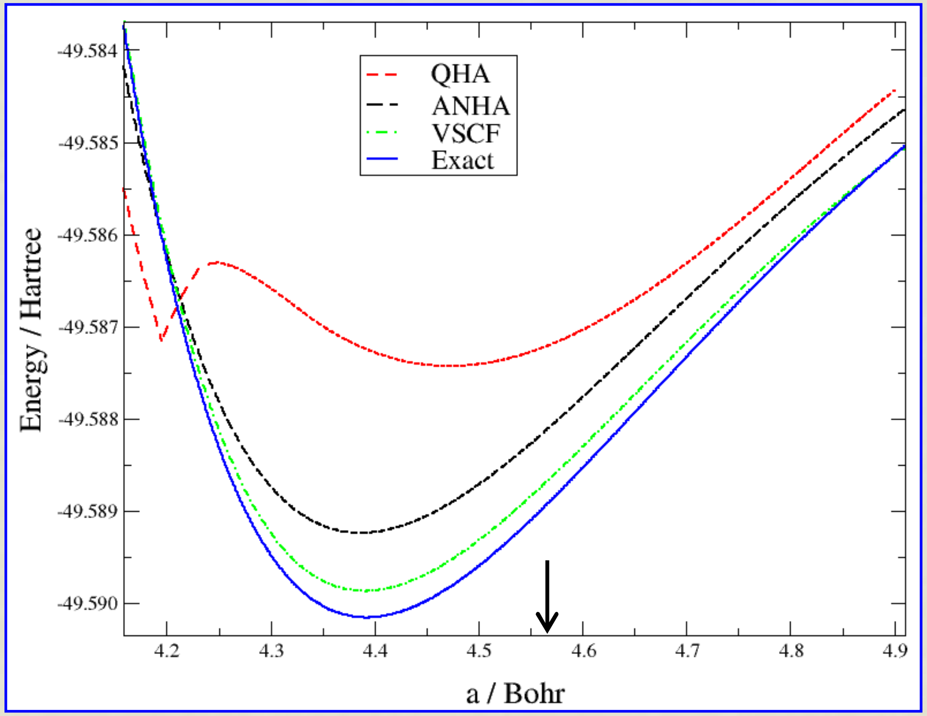
- QHA and ANH converge to same a for large N
- 1 cell (2 atoms) gives already a decent a.

2 cells (4 atoms): ANH, Exact and VSCF:

- ANH non-monotonic. OK for two cells
- a_{VSCF} is 0.04 Bohr smaller than a_{QHA}
- a_{Exact} is only 0.002 Bohr from a_{VSCF}

First-principles (DFT-GGA) linear HF chain

I. Scivetti, N. Gidopoulos and J. Kohanoff, Phys. Rev. B **78**, 224108 (2008)



Level	*a* (Å)
Class.	2.413
QHA	2.361
ANHA	2.321
VSCF	2.323
Exact	2.324

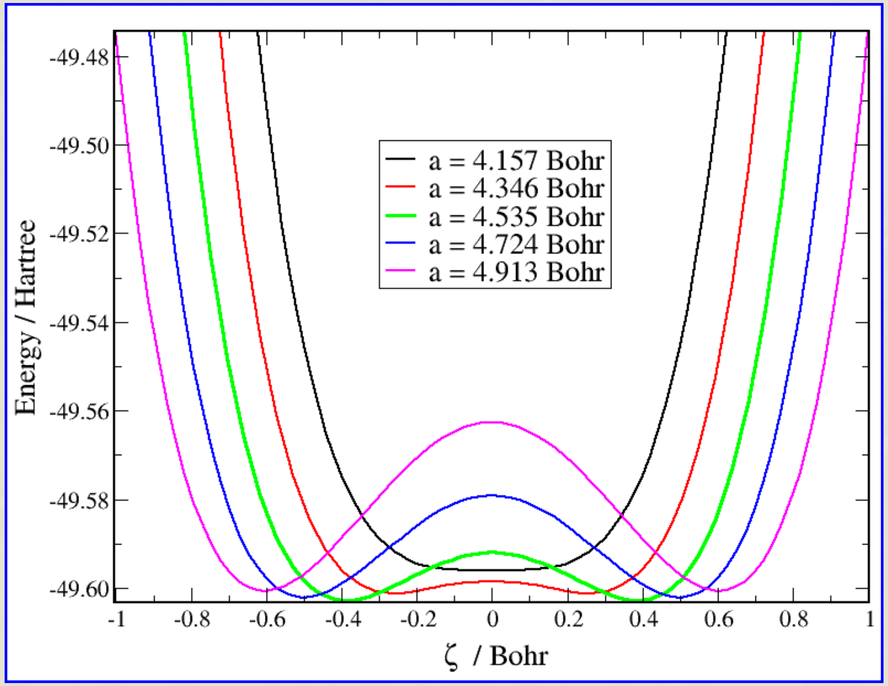
- a_{QHA} goes half way (Decrease 0.05 Å, but still 0.04 Å to go): **Anharmonicity is important**

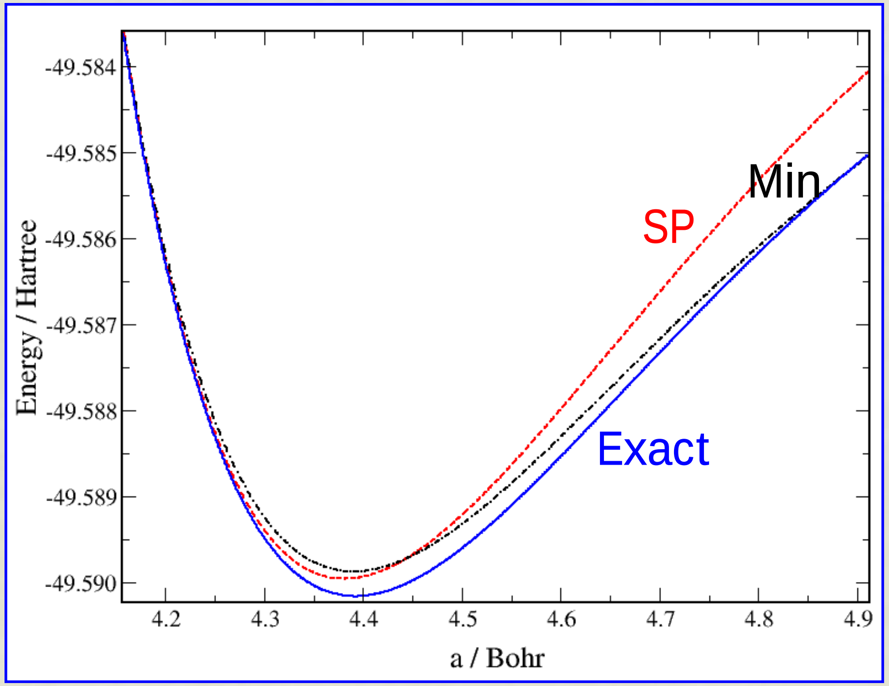
- a_{ANHA} appears to be quite good, and it is cheap! but ... is it reliable? (remember model)

- a_{Exact} and a_{VSCF} are indistinguishable: **Correlation between modes not very important**

First-principles (DFT-GGA) linear HF chain

Choice of vibrational coordinates

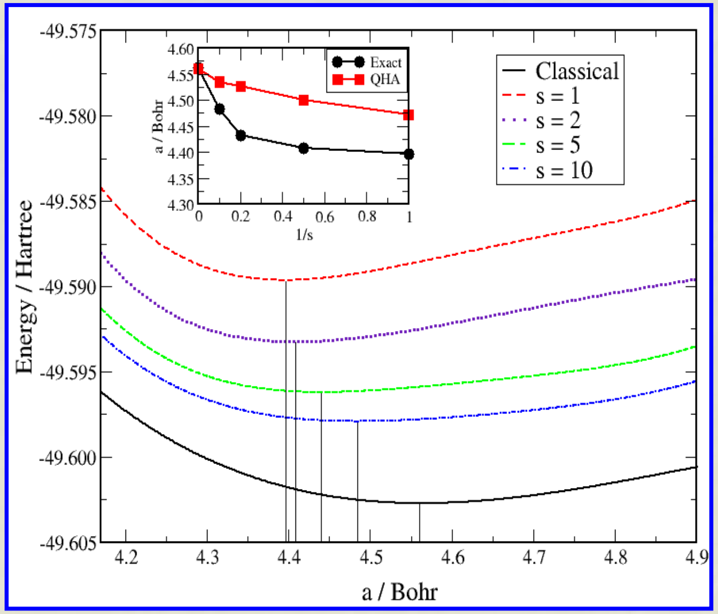




- Small a ⇒ no barrier ⇒ single anharmonic well ⇒ SP=Min are good.
- Large a ⇒ high barrier ⇒ wfn localized in Min ⇒ Min good, SP poor.
- Intermediate a ⇒ None is very good. Static correlation ⇒ Multiconfig.

First-principles linear HF chain

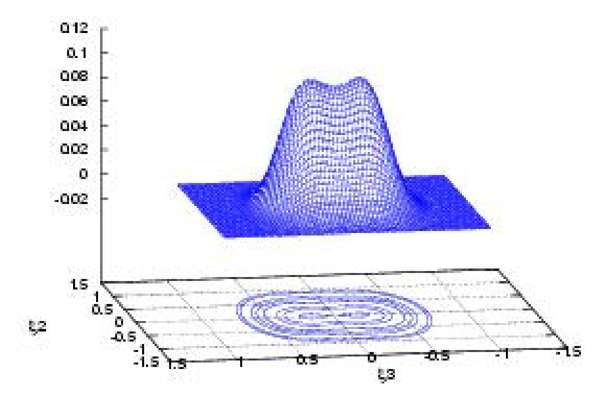
Isotope effect



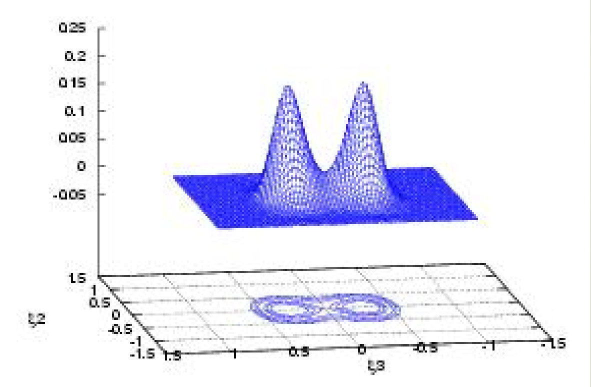
Internal Geometry

s	d_{FH} (Å)
∞	0.98
10	1.05
5	1.07
2	1.09
1	1.10

s=1



s=5



ZC and ZB optical modes

- Increasing m, a approaches the classical value

Lattice parameters are corrected

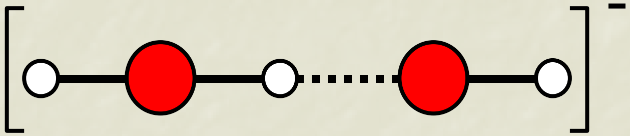
- Quantum-averaged F-H distance depends on m

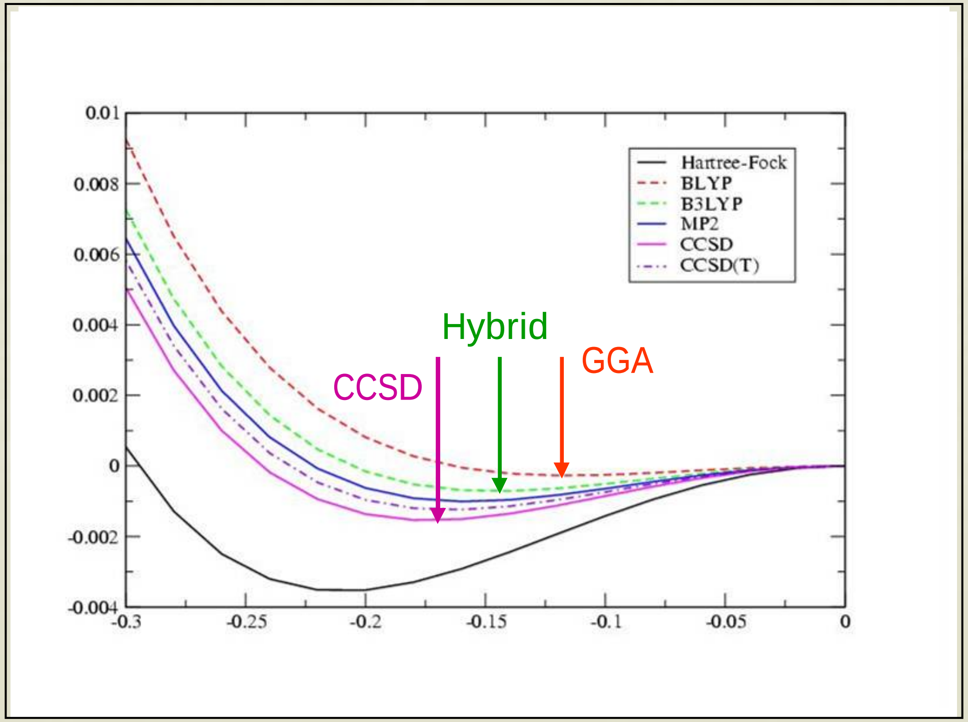
Internal geometry is also corrected

- **QHA overestimates lattice parameters**

Is DFT-GGA good enough for H-bonding?

A model H-bond: $O_2H_3^-$





- GGA severely underestimates barrier and finds minima too close to center

- MP2 underestimates and CCSD overestimates, but they are quite good

- Hybrid B3LYP is in between.

- Tweaked hybrid HF-DFT (MPWB1K) or Screened exchange can do a good job.

[Zhao and Truhlar, J. Phys. Chem. A **108**, 6908 (2004)]

[Heyd, Scuseria and Ernzerhof, JCP **118**, 8207 (2003)]

Conclusions

1. QHA quite safe to obtain quantum-corrected lattice parameters in covalently-bonded systems.
   - Coarse BZ sampling (4 or even 2 cells) is sufficient
2. QHA does not correct internal geometry at fixed cell.
   - Therefore, it does only half of the job in H-bonded systems.
3. ANHA seems quite good, but could be a size effect!
4. VSCF is an excellent approximation for structural properties.
   - Anharmonicity is important,
   - Correlation between modes is not necessarily relevant.
5. Careful with functionals for H-bonded systems!!