Phonon wavefunctions and electron–phonon interactions in semiconductors

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Quantum Monte Carlo in the Apuan Alps VII

Outline

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Motivation

Atomic motion plays an essential role:

- Total energy (ZPM, high temperatures, . . .)
- Thermal expansion (phonon pressure)
- Structural phase transitions (unstable phonons)
- Superconductivity (electron–phonon interactions)
- . . .

Anharmonicity is important for:

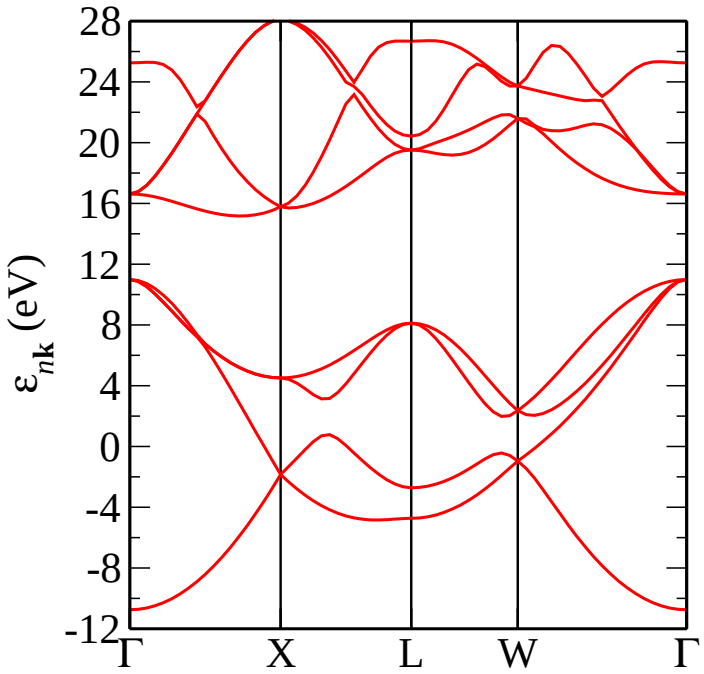
- High temperatures
- Light elements

Example: diamond band gap renormalisation

Diamond direct band gap:

- Experiment: 7.1 eV [1]
- DFT: 5.6 eV
- QMC: 7.2 eV [2]
- GW: 7.7 eV [3]

Differences ~ 0.1 eV



[1] S. Logothetidis, J. Petalas, H. M. Polatoglou, and D. Fuchs, Phys. Rev. B **46**, 4483 (1992)

[2] M. D. Towler, R. Q. Hood, and R. J. Needs, Phys. Rev. B **62**, 2330 (2000)

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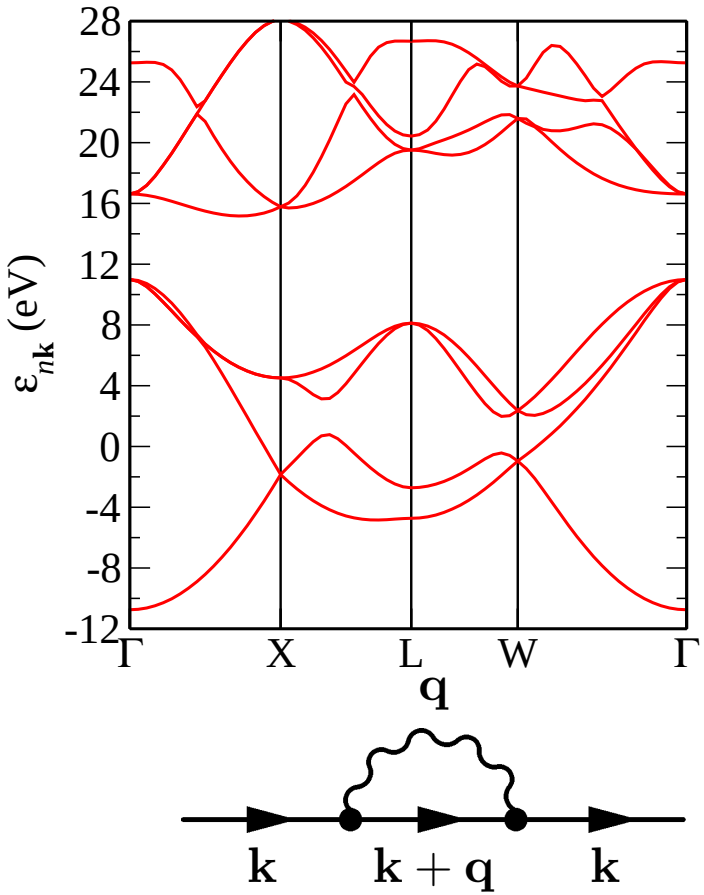
Electron–phonon interaction:
renormalisation of -0.6 eV



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Born–Oppenheimer approximation

Trial wavefunction: $\Psi_m(\{\mathbf{r}_i\},\{\mathbf{r}_\alpha\}) = \psi_m(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\})\Phi(\{\mathbf{r}_\alpha\})$
Equations of motion:

$$\begin{aligned}\hat{H}_e\psi_m(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\}) &= \epsilon_m(\{\mathbf{r}_\alpha\})\psi_m(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\}) \\ \hat{H}_n\Phi(\{\mathbf{r}_\alpha\}) &= E\Phi(\{\mathbf{r}_\alpha\})\end{aligned}$$

Hamiltonians:

$$\begin{aligned}\hat{H}_e &= -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_i\sum_\alpha \frac{Z_\alpha}{|\mathbf{r}_i-\mathbf{r}_\alpha|} \\ &\quad + \frac{1}{2}\sum_\alpha\sum_{\beta\neq\alpha}\frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|} \\ \hat{H}_n &= -\frac{1}{2}\sum_\alpha \frac{1}{m_\alpha}\nabla_\alpha^2 + \epsilon_m(\{\mathbf{r}_\alpha\})\end{aligned}$$

Harmonic approximation

Vibrational Hamiltonian in $\{\mathbf{r}_\alpha\}$ (or $\{\mathbf{u}_\alpha\}$):

$$\hat{H}_n = -\frac{1}{2}\sum_\alpha \frac{1}{m_\alpha}\nabla_\alpha^2 + \sum_{\alpha\beta} \mathbf{u}_\alpha \mathbf{D}_{\alpha\beta}\mathbf{u}_\beta$$

Normal mode analysis: $\{\mathbf{r}_\alpha\} \longrightarrow \{q_i\}$

Vibrational Hamiltonian in $\{q_i\}$:

$$\hat{H}_n = \sum_i \left(-\frac{1}{2}\frac{\partial^2}{\partial q_i^2} + \frac{1}{2}\omega_i^2 q_i^2 \right)$$

Vibrational self–consistent field equations

Phonon Schrödinger equation:

$$\left(\sum_{i=1}^{3N} -\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + V(\{q_i\}) \right) \Phi(\{q_i\}) = E\Phi(\{q_i\})$$

Ground state ansatz: $\Phi(\{q_i\}) = \prod_i \phi_i(q_i)$
Self–consistent equations:

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \overline{V}_i(q_i) \right) \phi_i(q_i) = \epsilon_i \phi_i(q_i)$$

$$\overline{V}_i(q_i) = \left\langle \prod_{j \neq i}^{3N} \phi_j(q_j) \middle| V(\{q_k\}) \middle| \prod_{j \neq i}^{3N} \phi_j(q_j) \right\rangle$$

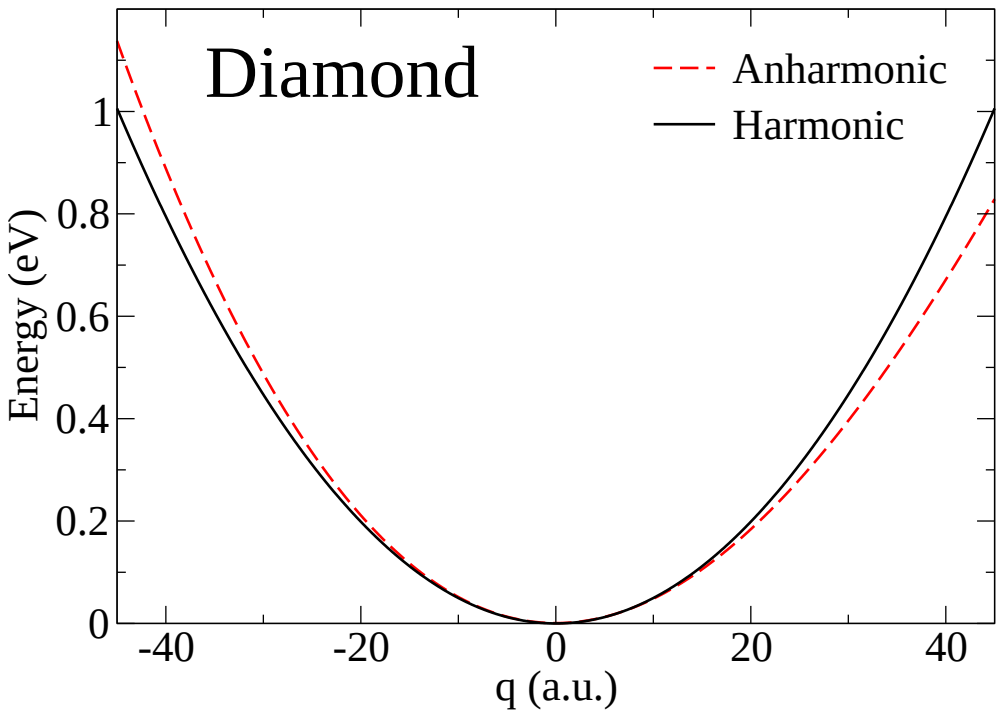
Approximating the Born–Oppenheimer energy surface (I)

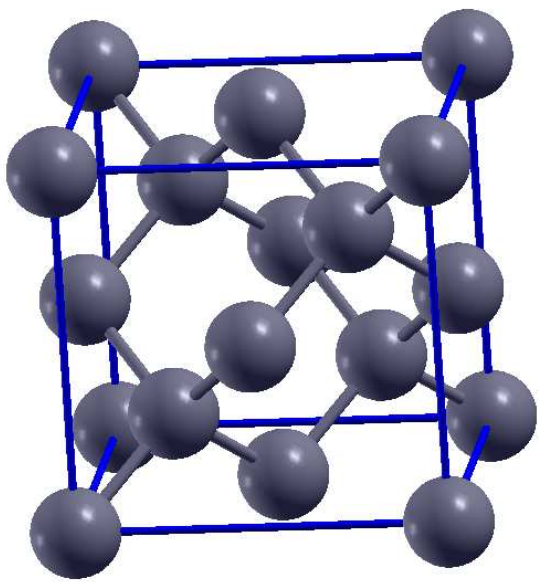
$$V(\{q_i\}) = V(0) + \sum_{i=1}^{3N} V_i(q_i) + \sum_{i=1}^{3N} \sum_{j>i}^{3N} V_{ij}(q_i, q_j) + \cdots$$

- Static lattice DFT total energy
- DFT total energy along frozen independent phonon
- DFT total energy along frozen coupled phonons

Approximating the Born–Oppenheimer energy surface (II)

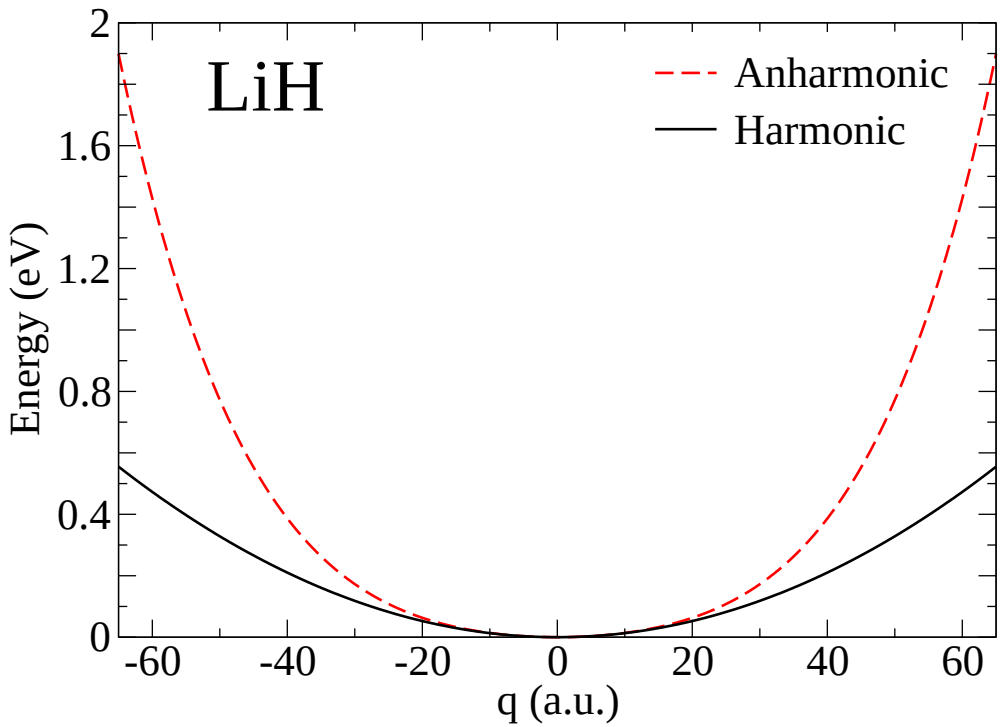
$$V(\{q_i\}) = V(0) + \sum_{i=1}^{3N} V_i(q_i) + \sum_{i=1}^{3N}\sum_{j>i}^{3N} V_{ij}(q_i, q_j) + \cdots$$

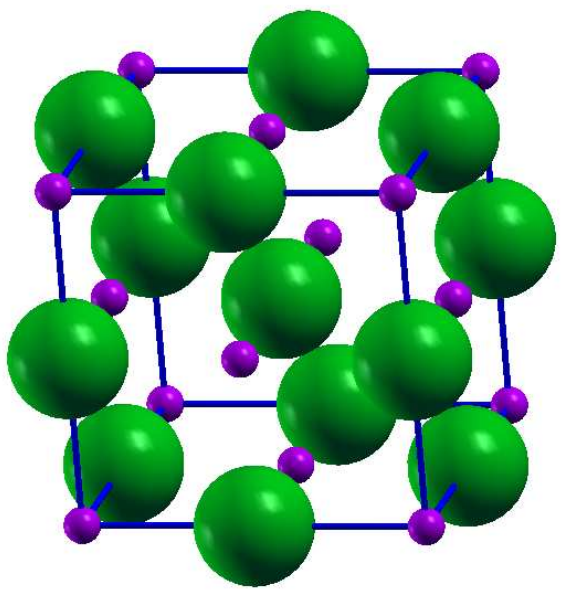




Approximating the Born–Oppenheimer energy surface (III)

$$V(\{q_i\}) = V(0) + \sum_{i=1}^{3N} V_i(q_i) + \sum_{i=1}^{3N}\sum_{j>i}^{3N} V_{ij}(q_i, q_j) + \cdots$$





Methodology

1. Supercell with N atoms $\rightarrow 3N$ normal modes
2. Solve for harmonic U_{har} and anharmonic U_{anh} energies
3. Calculate anharmonic correction $\Delta U_{anh} = U_{anh} - U_{har}$
4. Supercell size convergence for ΔU_{anh}
5. Add converged ΔU_{anh} to accurate harmonic energy

Phonon expectation values

Ground state ($T = 0$ K)

$$\begin{aligned}\langle \hat{A}(\{q_i\})\rangle_\Phi &= \langle \Phi(\{q_i\})|\hat{A}(\{q_i\})|\Phi(\{q_i\})\rangle \\ &= \int dq_1 \cdots \int dq_{3N}\, \Phi^*(\{q_i\})\hat{A}(\{q_i\})\Phi(\{q_i\})\end{aligned}$$

Finite temperature ($T > 0$ K)

$$\langle \hat{A}(\{q_i\})\rangle_{\Phi,\beta} = \frac{1}{\mathcal{Z}}\sum_s \langle \Phi_s(\{q_i\})|\hat{A}(\{q_i\})|\Phi_s(\{q_i\})\rangle e^{-\beta E_s}$$

$\hat{A}(\{q_i\})$ can be electronic band structure, stress tensor, ...

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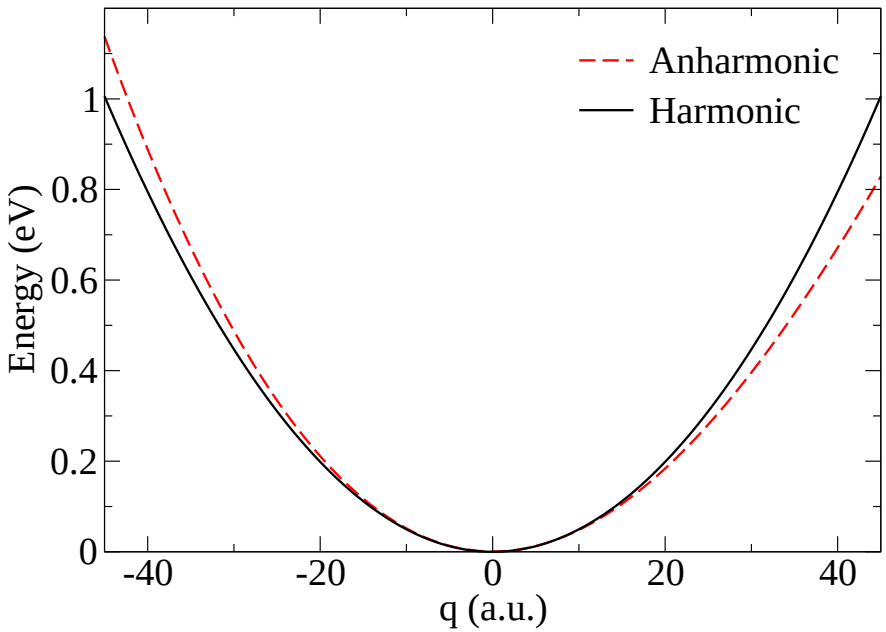
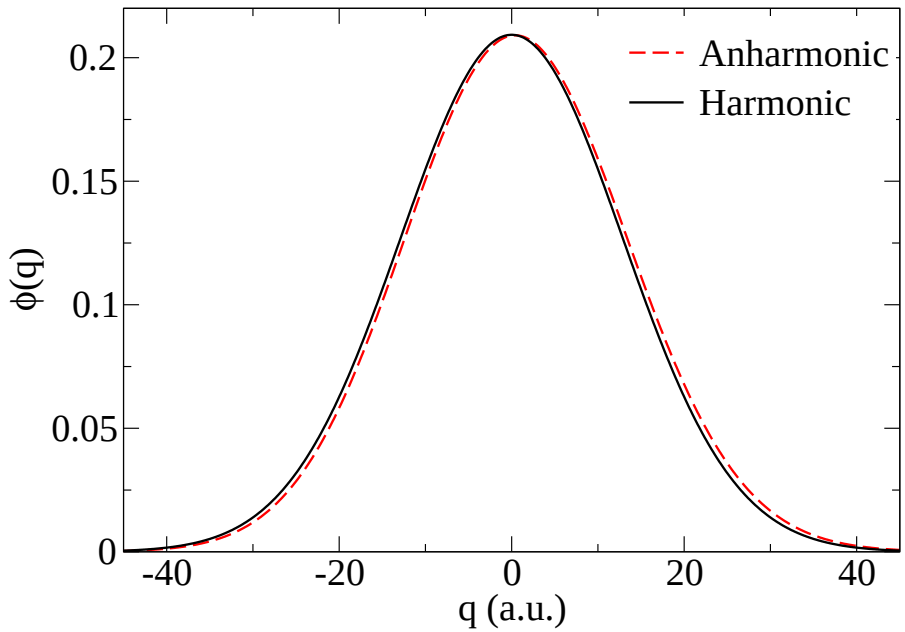
Diamond potential and phonon wavefunction



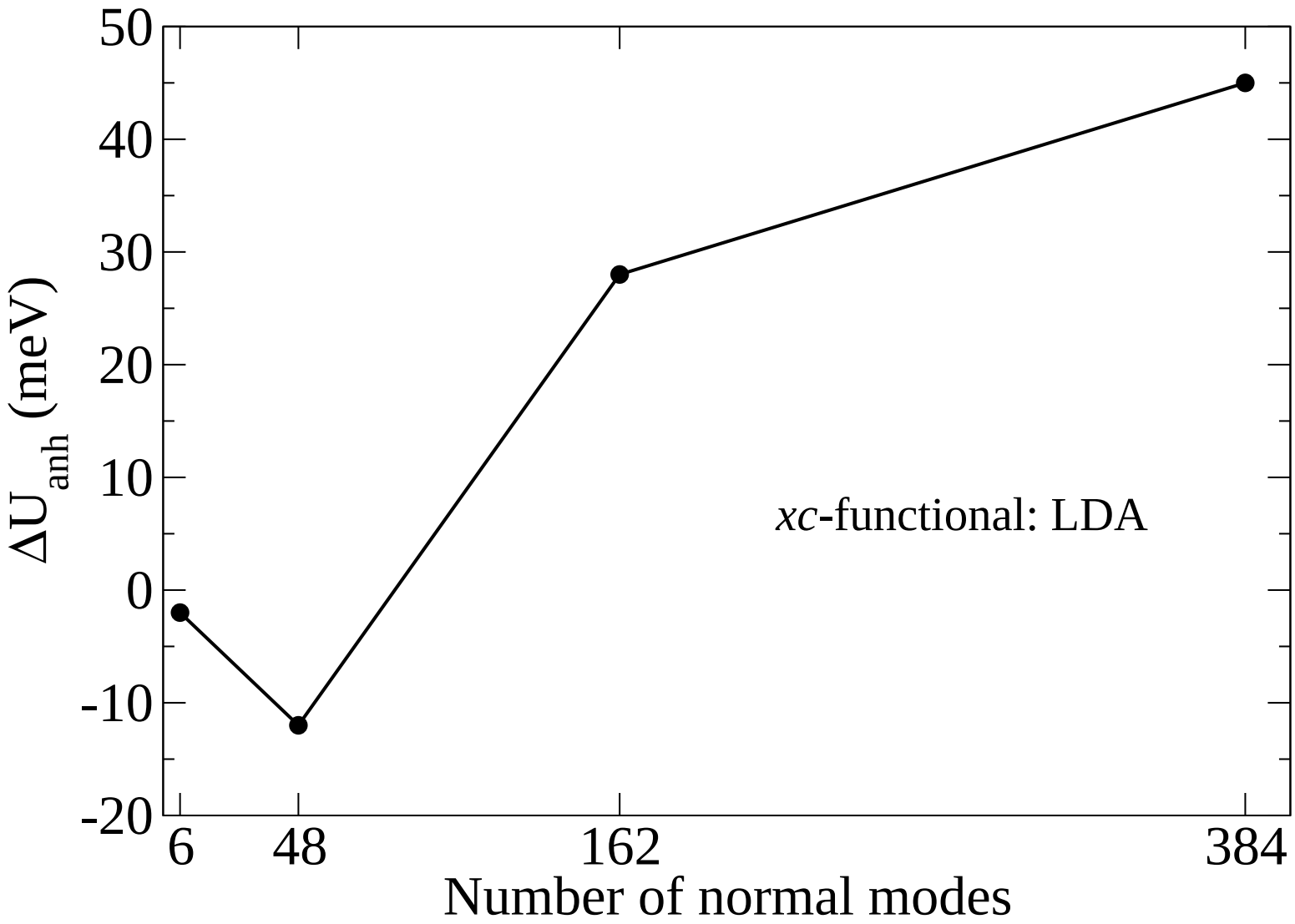


Diamond anharmonic ZPE (I)

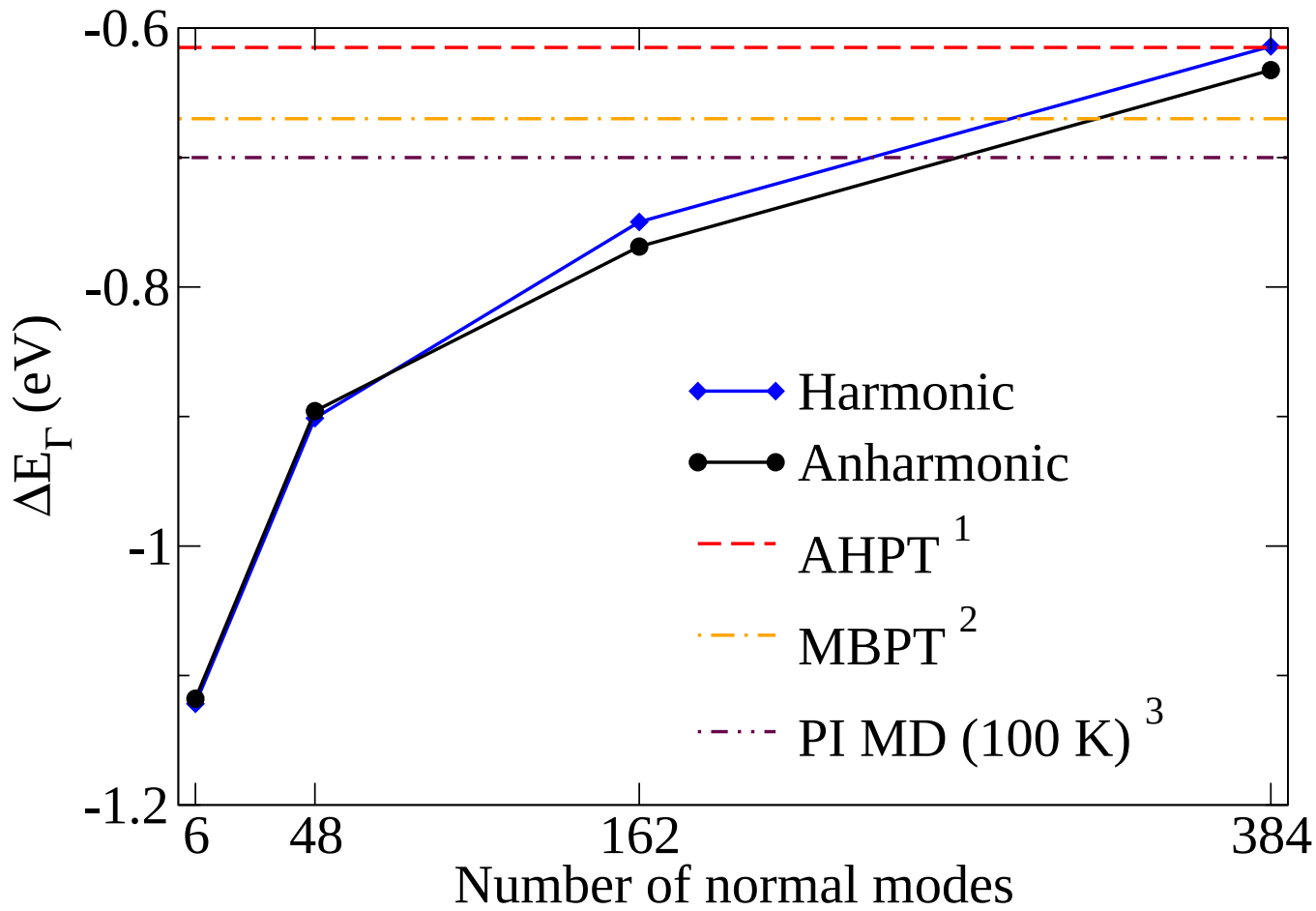
SC size	U_{har} (eV)	U_{anh} (eV)	ΔU_{anh} (eV)
Unit cell	0.251	0.249	-0.002
$2 \times 2 \times 2$	0.275	0.263	-0.012
$3 \times 3 \times 3$	0.282	0.310	$+0.028$
$4 \times 4 \times 4$	0.284	0.329	$+0.045$
$5 \times 5 \times 5$	0.286		
Accurate	0.368		

xc-functional: LDA

Diamond anharmonic ZPE (II)



Diamond Γ–point el–ph renormalisation



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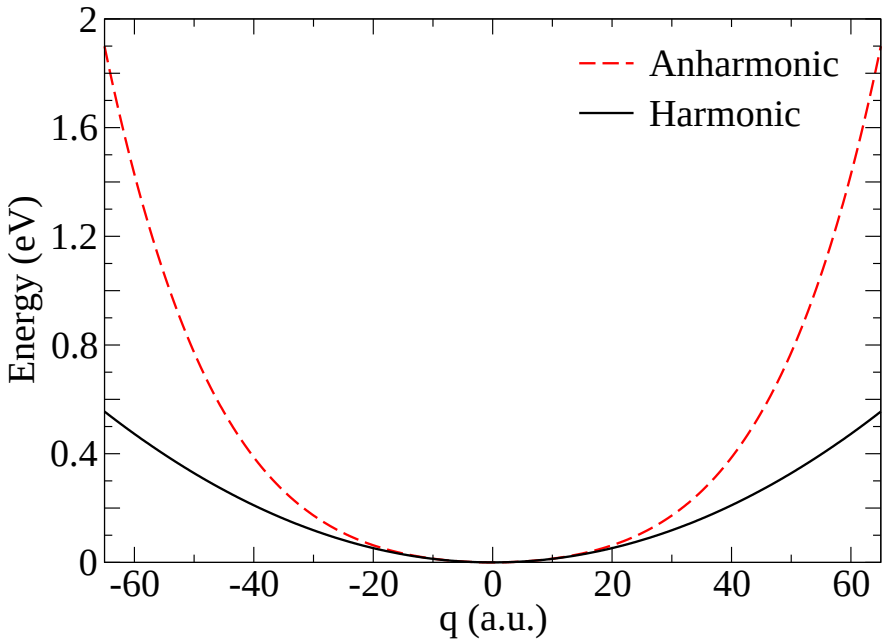
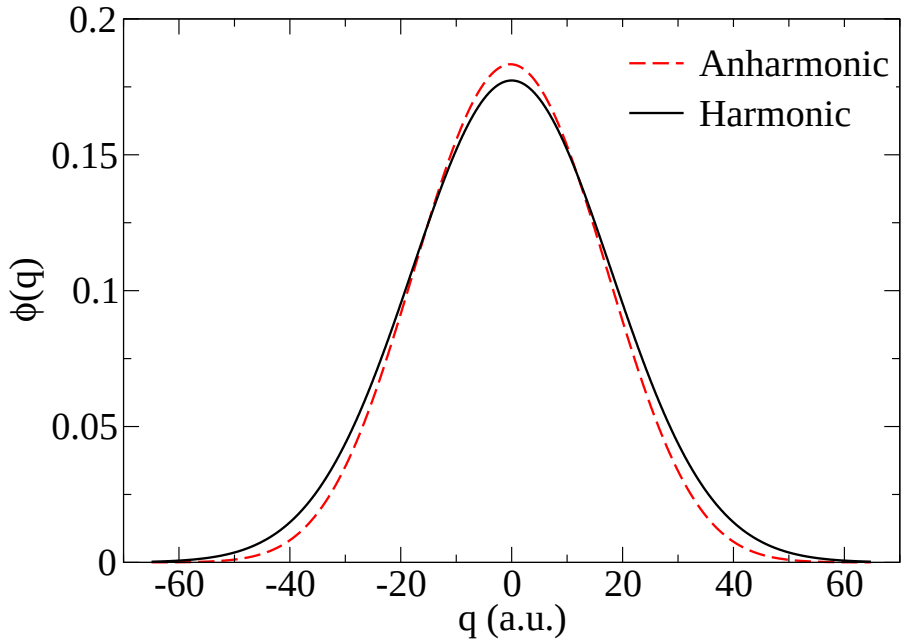
LiH potential and phonon wavefunction





LiH anharmonic ZPE (I)

E_{xc}	H	Li	U_{har} (eV)	U_{anh} (eV)	ΔU_{anh} (eV)
LDA	1	6	0.1455	0.1544	+0.0089
	1	7	0.1431	0.1509	+ 0.0078
	2	6	0.1131	0.1191	+0.0060
	2	7	0.1104	0.1144	+0.0040
PBE	1	6	0.1316	0.1400	+ 0.0084
	1	7	0.1294	0.1374	+ 0.0080
	2	6	0.1024	0.1074	+0.0050
	2	7	0.0999	0.1047	+ 0.0048

Supercell size: 48 modes

LDA lattice parameter: 3.665 bohr $\longrightarrow$ stiffer phonons

PBE lattice parameter: 3.780 bohr $\longrightarrow$ softer phonons

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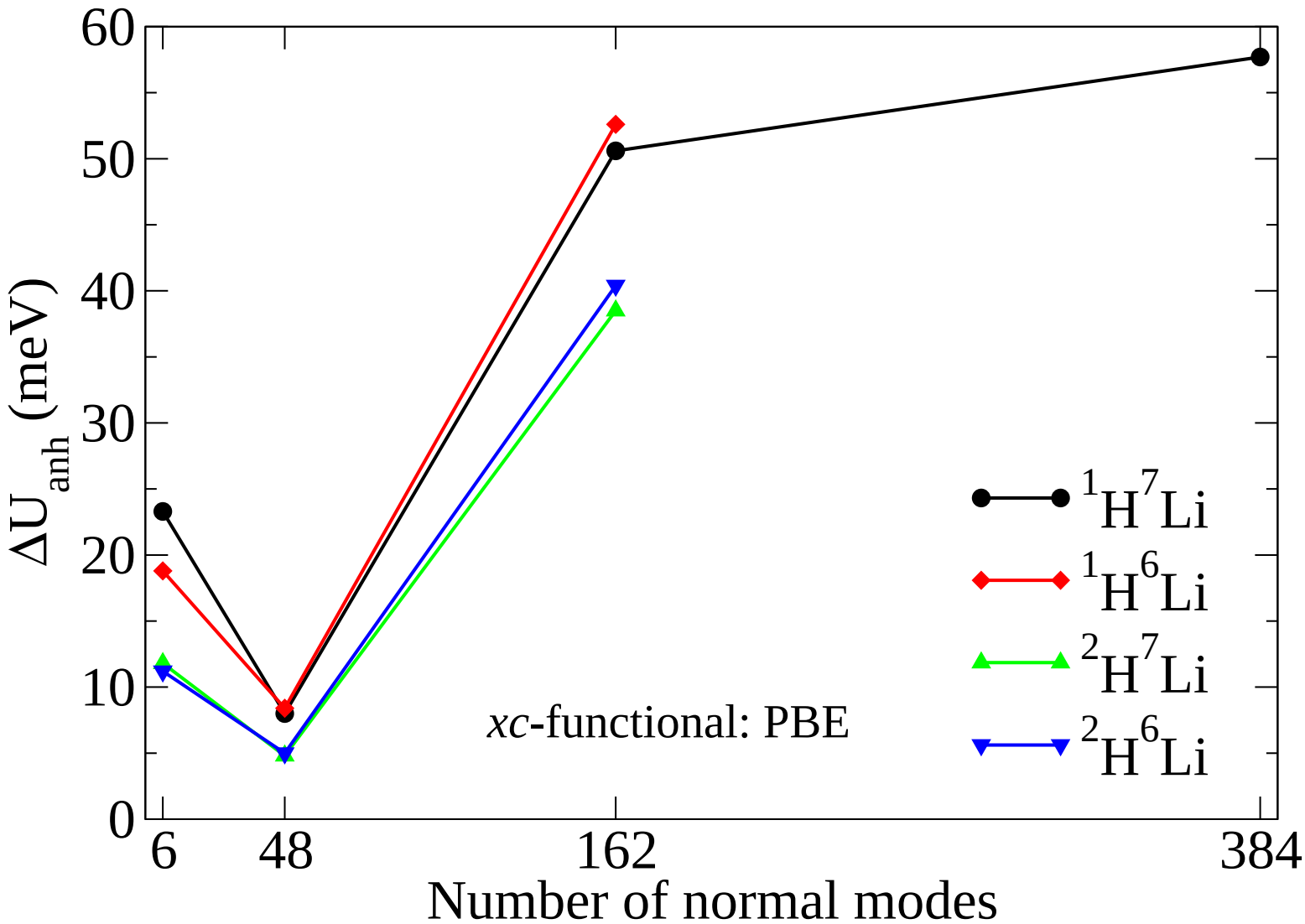
LiH anharmonic ZPE (II)

H	Li	U_{har} (eV)	U_{anh} (eV)	ΔU_{anh} (eV)
1	6	0.1365	0.1891	+0.0526
1	7	0.1342	0.1848	+0.0506
2	6	0.1062	0.1466	+0.0404
2	7	0.1037	0.1422	+0.0385

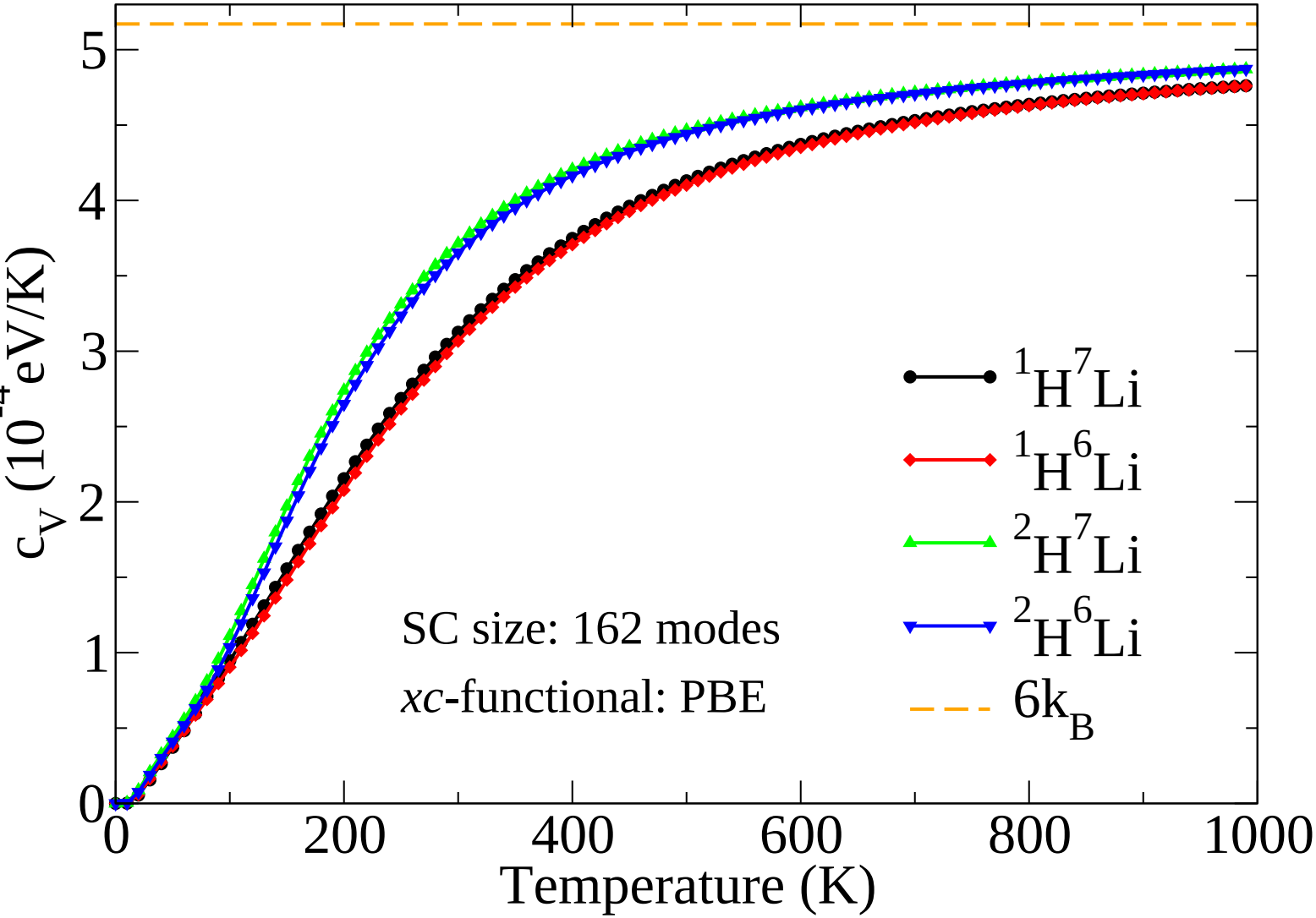
Supercell size: 162 modes

xc–functional: PBE

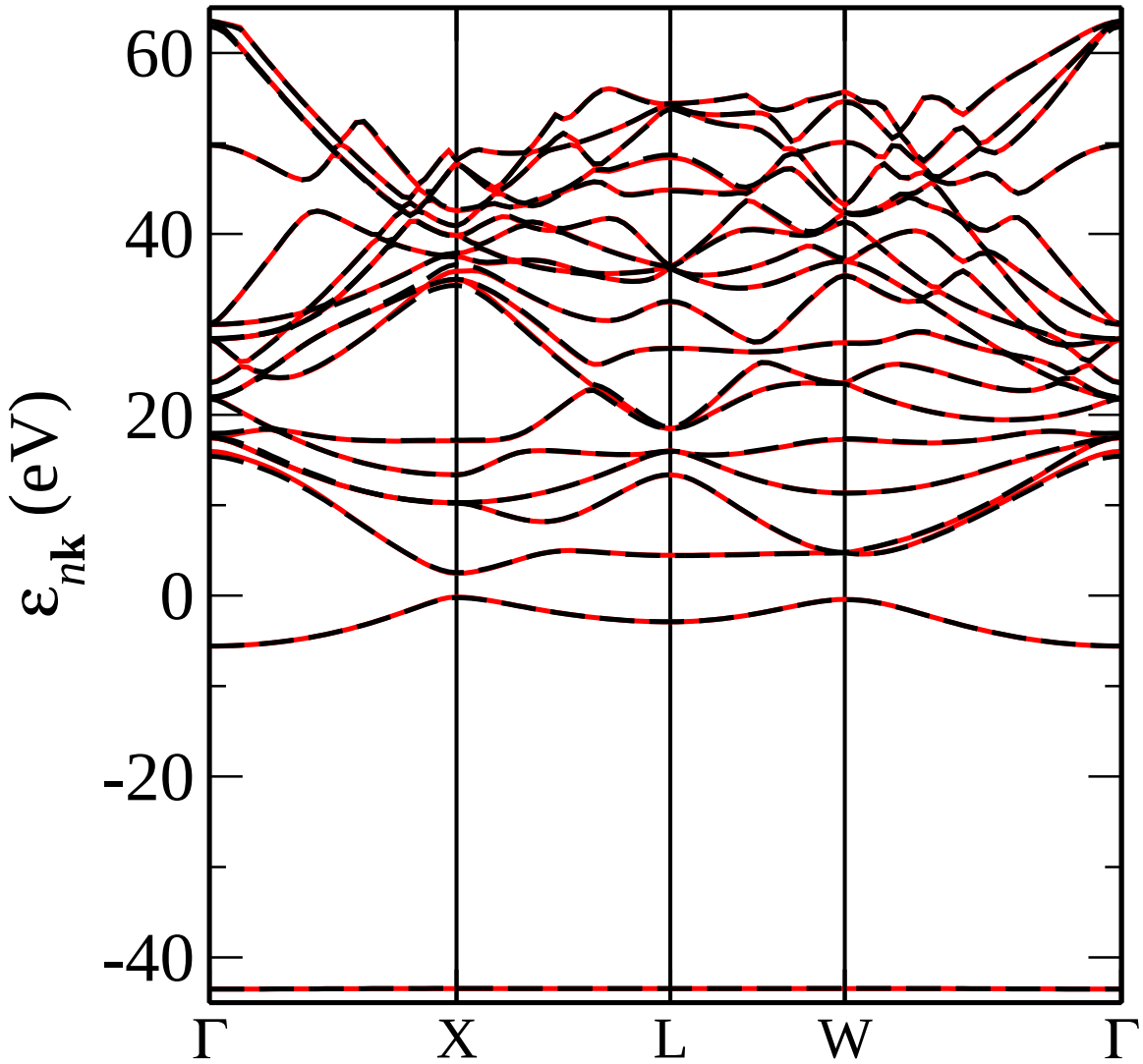
LiH anharmonic ZPE (III)



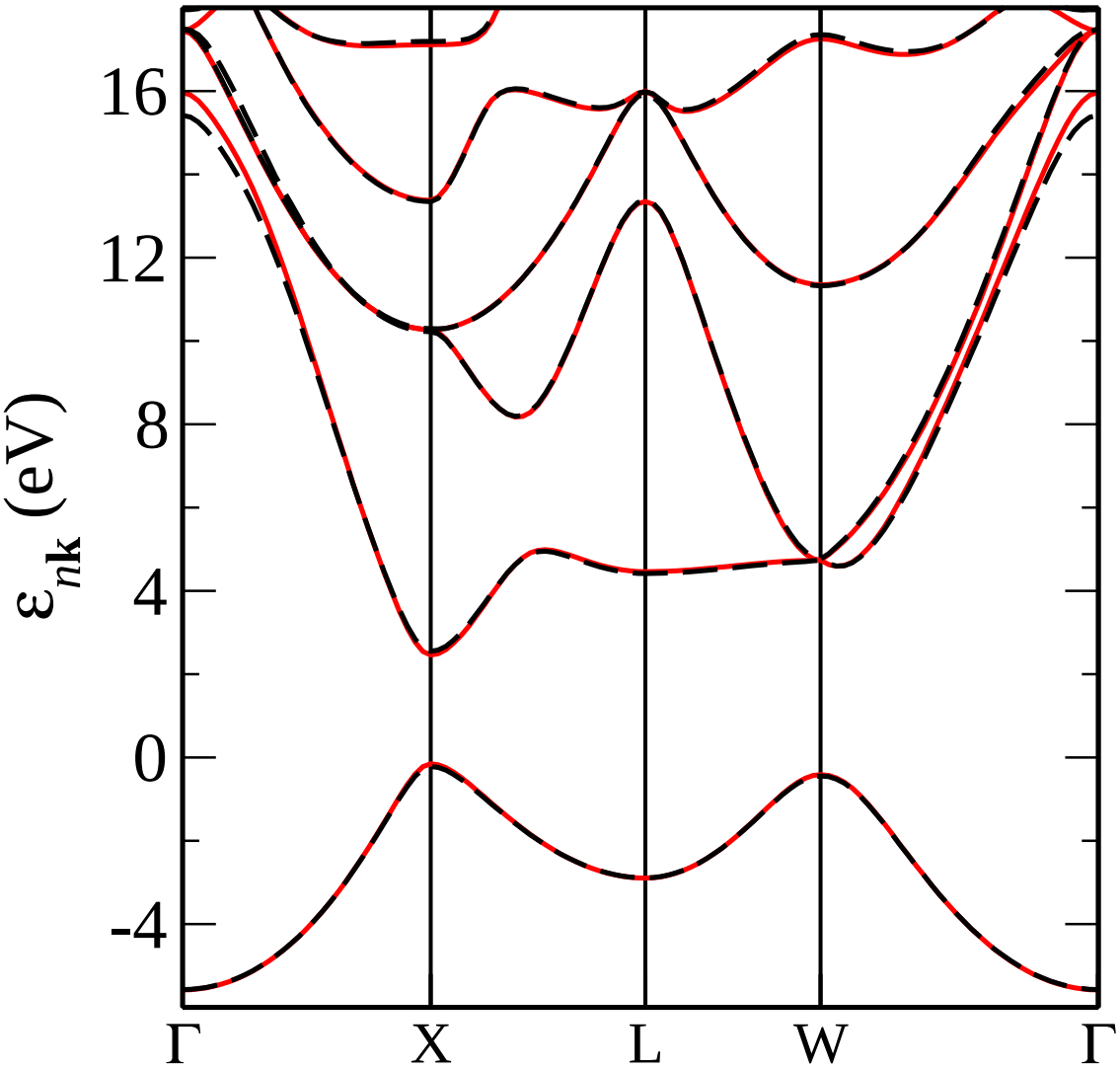
LiH constant volume heat capacity



El–ph renormalised LiH band structure (I)



El–ph renormalised LiH band structure (II)



LiH el–ph band gap renormalisations

H	Li	E_X (eV)	ΔE_X (eV)
1	7	3.0321	+0.0354
2	7	3.0289	+0.0319
Static lattice		2.9967	

Supercell size: 162 modes

xc–functional: PBE

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Conclusions

Summary:

- VSCF for phonon wavefunctions of bulk materials.
- Phonon expectation values for electronic band structure.
- Preliminary tests on diamond and LiH.

Future work:

- Other expectation values: stress tensor, atomic positions, ...
- Ice, solid hydrogen, ...

Acknowledgements

- Prof Richard J. Needs
- Dr Neil D. Drummond
- TCM group
- EPSRC

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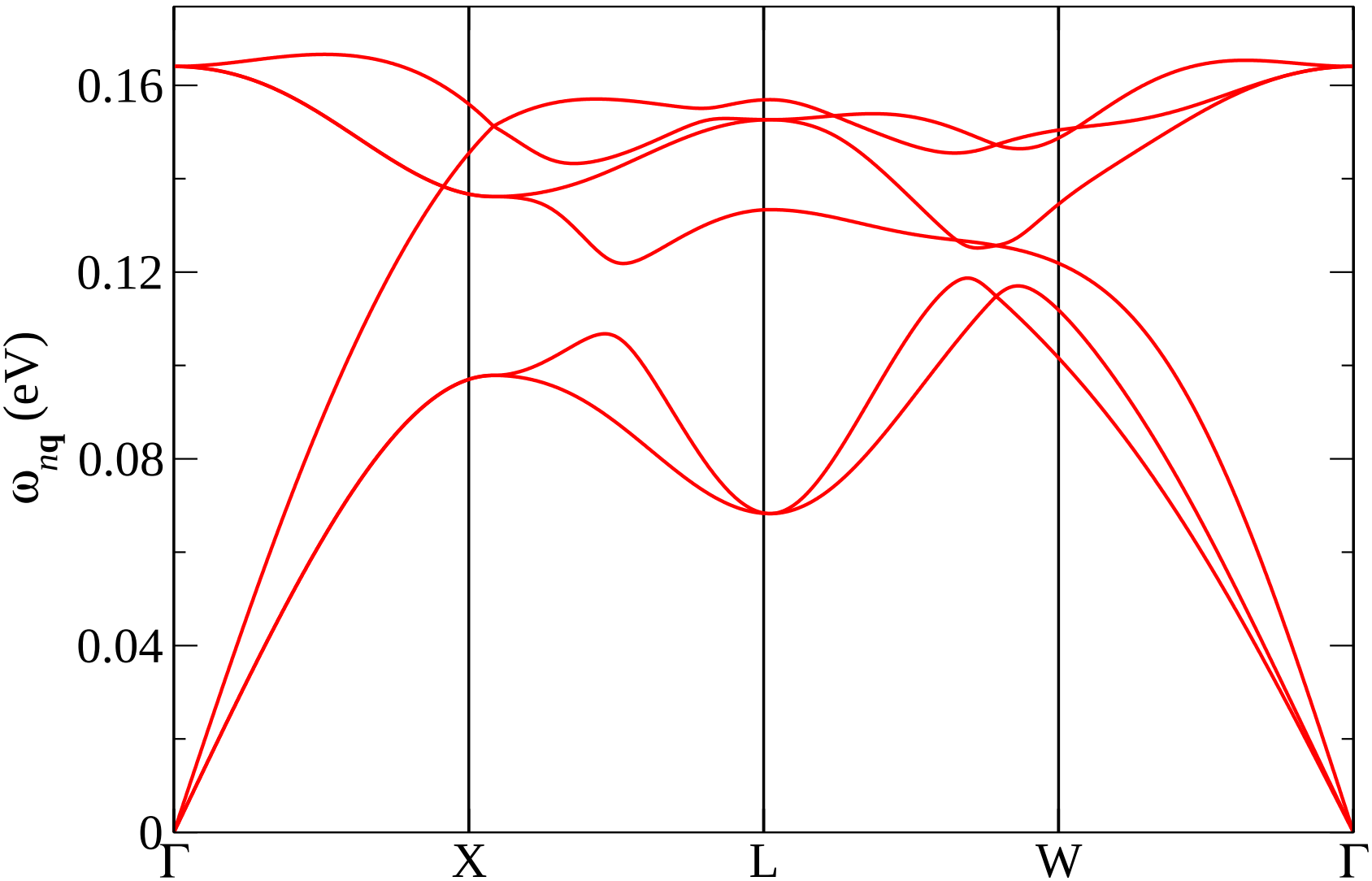
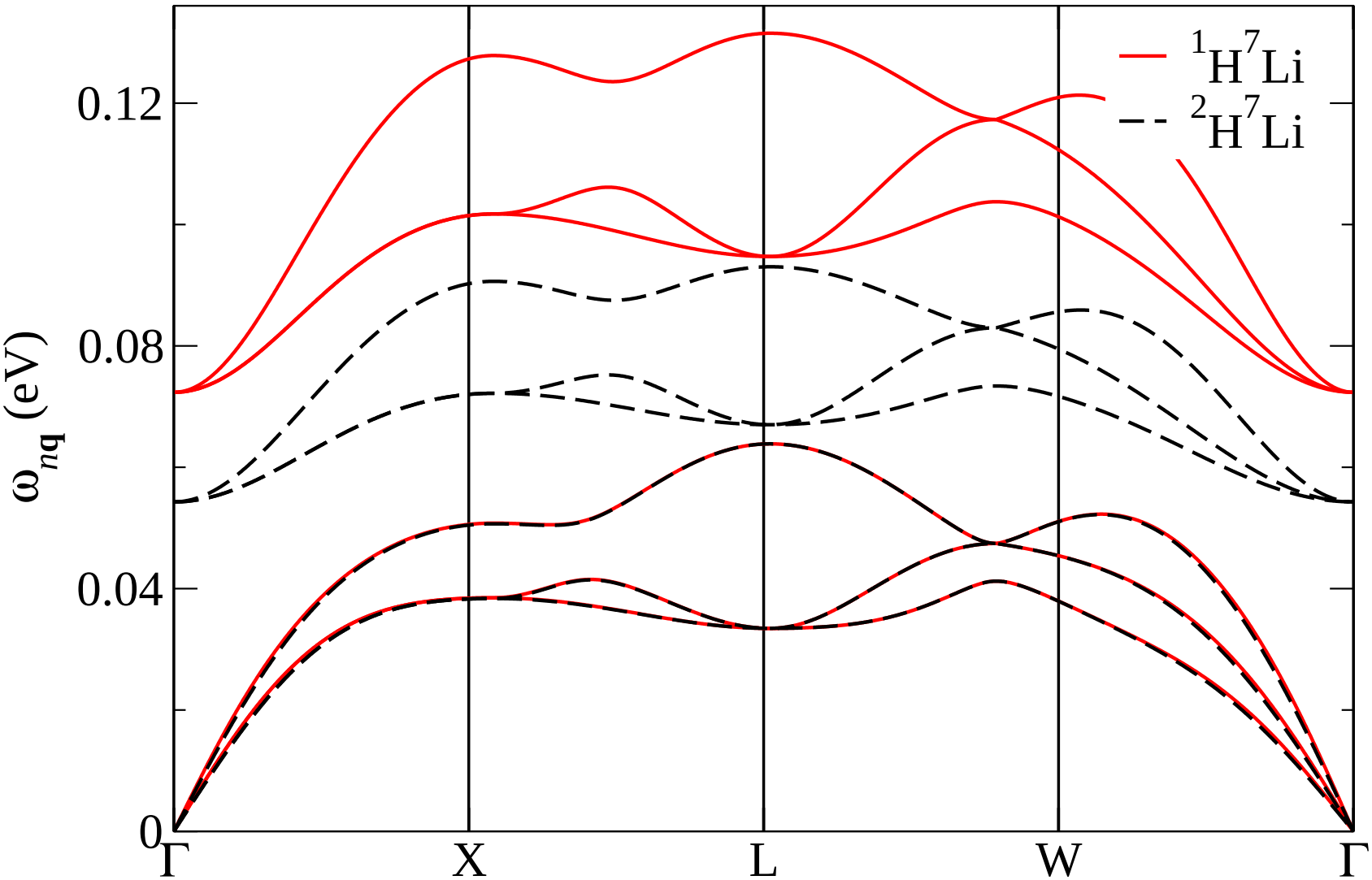
Additional Material: diamond phonon dispersion

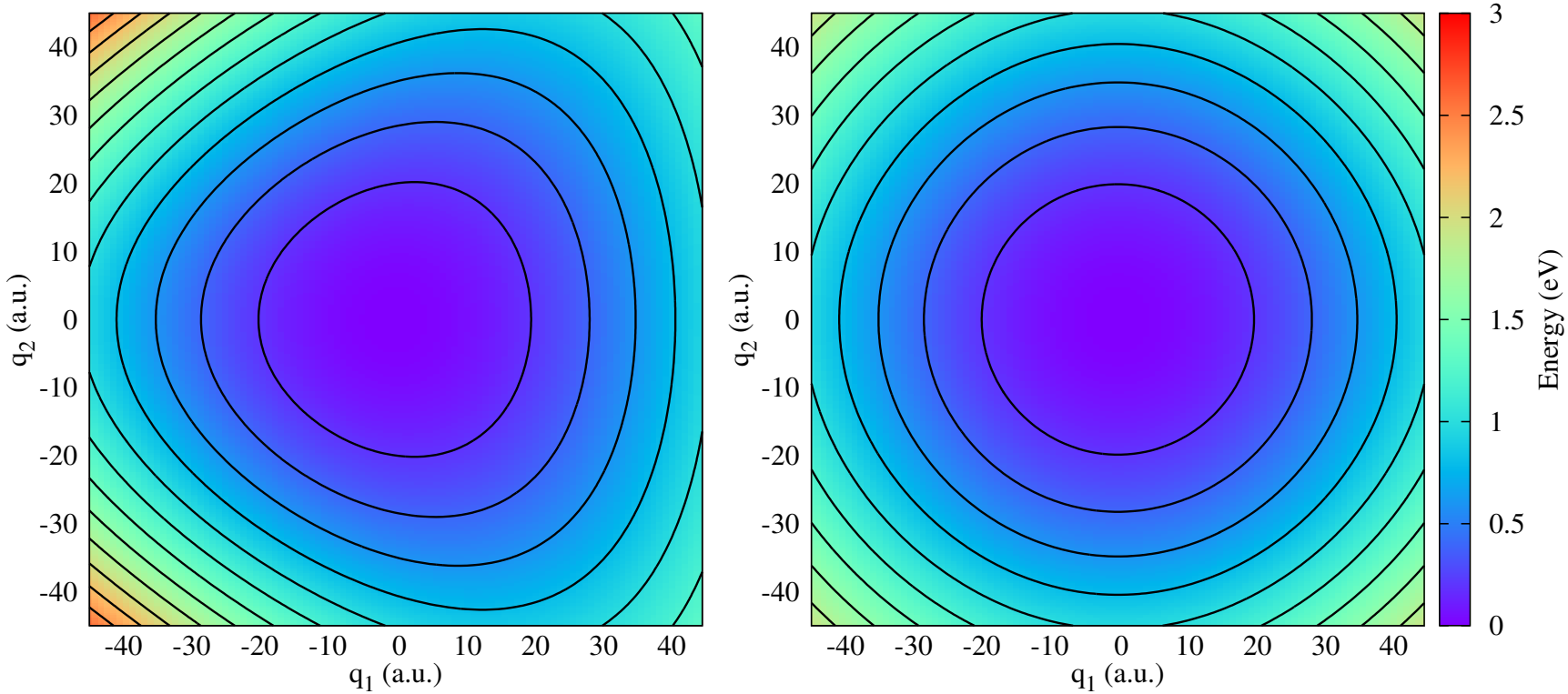


Additional Material: LiH phonon dispersion



Additional Material: Diamond coupling term

Coupled optical phonons at the Γ–point



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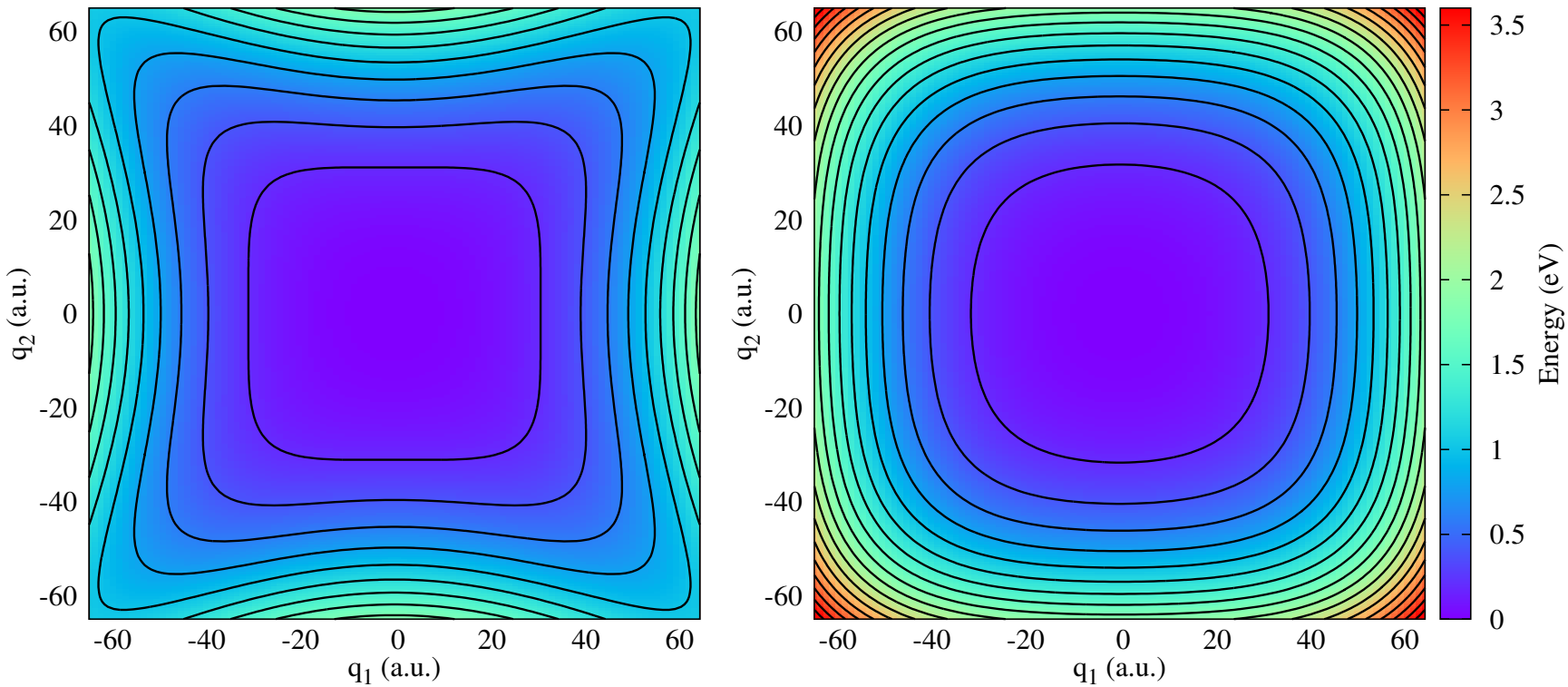

Additional Material: Allen–Heine perturbation theory (I)

Expansion of el–ph interaction to second order in $\mathbf{u}_\alpha$:

$$V_{\mathrm{el-ph}}(\{\mathbf{u}_\alpha\}) \simeq \hat{H}_1 + \hat{H}_2$$
$$\hat{H}_1 = \sum_\alpha \mathbf{u}_\alpha \nabla_\alpha V_{\mathrm{el-ph}}(\{\mathbf{u}_\alpha\})$$
$$\hat{H}_2 = \frac{1}{2} \sum_{\alpha\beta} \mathbf{u}_\alpha \mathbf{u}_\beta \nabla_\alpha \nabla_\beta V_{\mathrm{el-ph}}(\{\mathbf{u}_\alpha\})$$

Second order perturbation theory:

$$\epsilon_{n\mathbf{k}}(\{\mathbf{u}_\alpha\}) \simeq \epsilon_{n\mathbf{k}} + \langle n\mathbf{k}|\hat{H}_1 + \hat{H}_2|n\mathbf{k}\rangle + \sum_{n'\mathbf{k}'} \frac{|\langle n'\mathbf{k}'|\hat{H}_1|n\mathbf{k}\rangle|^2}{\epsilon_{n\mathbf{k}} - \epsilon_{n'\mathbf{k}'}}$$

Additional Material: Allen–Heine perturbation theory (II)

Thermal average within harmonic approximation (reciprocal space):

$$\frac{1}{2m_\alpha N\omega_{\nu\mathbf{q}}}(2n_{\nu\mathbf{q}}+1)$$
$$n_{\nu\mathbf{q}} = \frac{1}{e^{\beta\omega_{\nu\mathbf{q}}}+1} \tag{1}$$