Electronic Structure: from BlackBoard to Source Code

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computing

betas and qs

for

NCPP/USPP/PAW PseudoPotentials

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle \beta_{lm}|r'\rangle$$

ab initio Norm Conserving PseudoPotentials

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$$\tilde{V}_{Z_v}^{PS} = \sum_{s,R} V_s^{loc}(|r-R-\tau_s|)\delta(r-r') + \sum_{s,R} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r-R-\tau_s|\beta_{lm}^s\rangle \, D_l^s \, \langle \beta_{lm}^s|r'-R-\tau_s\rangle$$

ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm}\rangle \, D_l \, \langle \beta_{lm}|r'\rangle$$

$$\tilde{V}_{Z_v}^{PS} = \sum_{s,R} V_s^{loc}(|r-R-\tau_s|)\delta(r-r') + \sum_{s,R} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r-R-\tau_s|\beta_{lm}^s\rangle \, D_l^s \, \langle \beta_{lm}^s|r'-R-\tau_s\rangle$$

$$\langle k+G|\tilde{V}_{Z_v}^{PS}|k+G'\rangle = \sum_s V_s^{loc}(|G-G'|)\, e^{-i(G-G')\tau_s} + \sum_{s} \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle k+G|\beta_{lm}^s\rangle e^{-iG\tau_s} \, D_l^s \, e^{iG'\tau_s} \langle \beta_{lm}^s|k+G'\rangle$$

$$\langle \mathbf{r} | \beta_{nlm} \rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{r}|\beta_{nlm}\rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = \int \frac{e^{-i\mathbf{kr}}}{\sqrt{\Omega}} \langle \mathbf{r}|\ \beta_{nlm}\rangle\ d\mathbf{r}$$

$$\langle \mathbf{r}|\beta_{nlm}\rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = \int \frac{e^{-i\mathbf{kr}}}{\sqrt{\Omega}} \langle \mathbf{r}|\ \beta_{nlm}\rangle\ d\mathbf{r}$$

$$exp[i\mathbf{kr}] = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y^*_{lm}(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{r}|\beta_{nlm}\rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = \int \frac{e^{-i\mathbf{kr}}}{\sqrt{\Omega}} \langle \mathbf{r}|\ \beta_{nlm}\rangle\ d\mathbf{r}$$

$$exp[i\mathbf{kr}] = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y^*_{lm}(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = \frac{4\pi}{\sqrt{\Omega}}\ (-i)^l \int_0^{\infty} j_l(kr) \tilde{\beta}^{at}_{nl}(r) r dr\ \ Y_{lm}(\hat{\mathbf{k}})$$

$$\langle \mathbf{r}|\beta_{nlm}\rangle = \frac{\tilde{\beta}^{at}_{nl}(r)}{r} Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = \int \frac{e^{-i\mathbf{kr}}}{\sqrt{\Omega}} \langle \mathbf{r}|\ \beta_{nlm}\rangle\ d\mathbf{r}$$

$$exp[i\mathbf{kr}] = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y^*_{lm}(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = \frac{4\pi}{\sqrt{\Omega}} (-i)^l \int_0^{\infty} j_l(kr) \tilde{\beta}^{at}_{nl}(r) r dr \ \ Y_{lm}(\hat{\mathbf{k}})$$

$$\langle \mathbf{k}|\beta_{nlm}\rangle = (-i)^l \ \tilde{\beta}^{at}_{nl}(k) \ \ Y_{lm}(\hat{\mathbf{k}})$$

with $$\tilde{\beta}^{at}_{ln}(k) = \frac{4\pi}{\sqrt{\Omega}} \int_0^{\infty} j_l(kr) \tilde{\beta}^{at}_{nl}(r) r dr$$

IF (.NOT. real_space) [default] :

init_us_1 (called in hinit0) computes a table of radial Bessel transforms from the atomic betas on the radial grid.

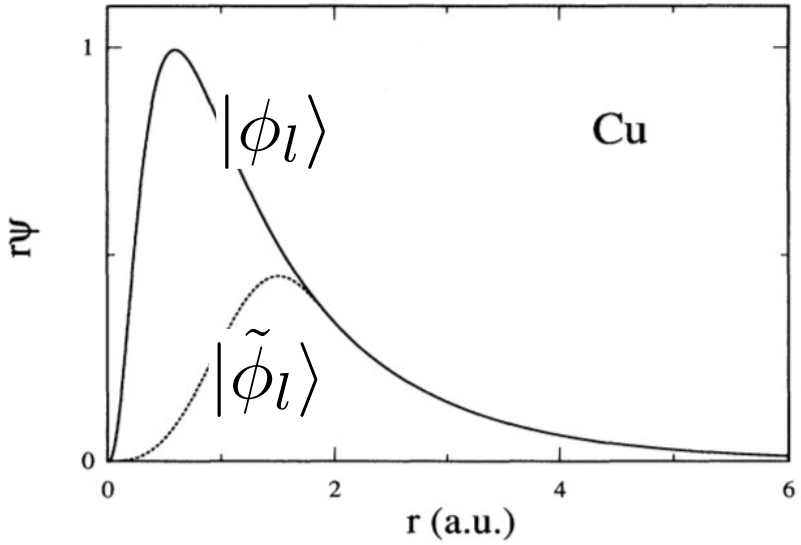
init_us_2 (called whenever the betas are needed) interpolates the table and assembles it with the needed Y_lm

IF (real_space) :

betapointlist & init_realspace_vars (called in hinit0) build atom-centered lists of real space points and spline interpolate the betas from the atomic radial grid (w the neeeded Y_lm)

Whenever needed integrals and wfc updates are performed only over the points of the above grids (calbec_rs_gamma/k, add_vuspsir_gamma/k, s_psir_gamma/k)

Ultra Soft PseudoPotentials



$$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_i \sum_{ll'} \langle \psi_i | \beta_l \rangle Q_{ll'}(r) \langle \beta_{l'} | \psi_i \rangle$$

where the "augmentation charges" are

$$Q_{ll'}(r) = \phi_l^*(r)\phi_l'(r) - \tilde{\phi}_l^*(r)\tilde{\phi}_l'(r)$$

$|\beta_l\rangle$ are projectors

$|\phi_l\rangle$ are atomic states (not necessarily bound)

$|\tilde{\phi}_l\rangle$ are pseudo-waves (coinciding with $|\phi_l\rangle$ beyond some *core radius*)

Ultra Soft PseudoPotentials

$$\hat{V}^{USPP} = V_{loc}(r) + \sum_{ll'} |\beta_l\rangle D^0_{ll'} \langle\beta_{l'}|$$

Orthogonality with USPP:

$$\langle\psi_i|S|\psi_j\rangle = \langle\psi_i|\psi_j\rangle + \sum_{ll'} \langle\psi_i|\beta_l\rangle q_{ll'} \langle\beta_{l'}|\psi_j\rangle = \delta_{ij}$$

where $$q_{ll'} = \int Q_{ll'}(r) dr$$

leading to a generalized eigenvalue problem

$$[H_{KS} - \varepsilon_i S] \ |\psi_i\rangle = 0$$

Ultra Soft PseudoPotentials

There are additional terms in the density, in the energy, in the hamiltonian in the forces, ...

$$E = \sum_i \langle \psi_i | \hat{T}_s + \hat{V}^{USPP} | \psi_i \rangle + E_{Hxc}[\rho] - \sum_{ij} \lambda_{ij} (\langle \psi_i | S | \psi_j \rangle - \delta_{ij})$$

where $$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_i \sum_{ll'} \langle \psi_i | \beta_l \rangle Q_{ll'}(r) \langle \beta_{l'} | \psi_i \rangle$$

$$\rho(r) = \sum_i |\psi_i(r)|^2 + \sum_s \sum_i \sum_{ll'} \langle \psi_i | \beta_l^s \rangle Q_{ll'}(r - \tau_s) \langle \beta_{l'}^s | \psi_i \rangle$$

$$\rho(G) = \tilde{\rho}(G) + \sum_s \sum_{ll'} \sum_i \langle \psi_i | \beta_l^s \rangle \langle \beta_{l'}^s | \psi_i \rangle \; Q_{ll'}^s(G) e^{-iG\tau_s}$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\, Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\, Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{G}) = \frac{1}{\Omega}\int e^{-i\mathbf{G}\mathbf{r}} Q_{nlm,n'l'm'}(\mathbf{r})\, d\mathbf{r}$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\, Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{G}) = \frac{1}{\Omega}\int e^{-i\mathbf{Gr}} Q_{nlm,n'l'm'}(\mathbf{r})\, d\mathbf{r}$$

$$Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}}) = \sum_{L=|l-l'|}^{l+l'} \alpha^{L}_{lm,l'm'}\, Y_{LM}(\hat{\mathbf{r}}), \qquad M = m + m'$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\, Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{G}) = \frac{1}{\Omega}\int e^{-i\mathbf{Gr}} Q_{nlm,n'l'm'}(\mathbf{r})\, d\mathbf{r}$$

$$Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}}) = \sum_{L=|l-l'|}^{l+l'} \alpha^{L}_{lm,l'm'}\, Y_{LM}(\hat{\mathbf{r}}), \qquad M = m + m'$$

$$exp[i\mathbf{Gr}] = 4\pi \sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l j_l(Gr) Y^*_{lm}(\hat{\mathbf{G}})Y_{lm}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{r}) = \frac{\tilde{Q}^{at}_{nl,n'l'}(r)}{r^2}\, Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}})$$

$$Q_{nlm,n'l'm'}(\mathbf{G}) = \frac{1}{\Omega}\int e^{-i\mathbf{G}\mathbf{r}} Q_{nlm,n'l'm'}(\mathbf{r})\, d\mathbf{r}$$

$$Y_{lm}(\hat{\mathbf{r}})Y_{l'm'}(\hat{\mathbf{r}}) = \sum_{L=|l-l'|}^{l+l'} \alpha^{L}_{lm,l'm'}\, Y_{LM}(\hat{\mathbf{r}}), \qquad M = m + m'$$

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$$Q_{nlm,n'l'm'}(\mathbf{G}) = \sum_{L=|l-l'|}^{l+l'} (-i)^L \alpha^{L}_{lm,l'm'}\;\; \tilde{Q}^{L}_{nl,n'l'}(G)\;\; Y_{Lm+m'}(\hat{\mathbf{G}})$$

with $$\tilde{Q}^{L}_{nl,n'l'}(G) = \frac{4\pi}{\Omega}\int_0^{\infty} j_L(Gr)\, \tilde{Q}^{at}_{nl,n'l'}(r)\, dr$$

IF (.NOT. tqr) [default] :

init_us_1 (called in hinit0) computes a table of radial Bessel transforms from the atomic qs on the radial grid.

qvan2 (called whenever a component of the augmentation charge is needed) interpolates the qs-table and assembles it with the needed Y_lm and alphas

IF (tqr) :

generate_qpointlist (called in hinit0) build atom-centered lists of real space points and spline interpolate the qs from the atomic radial grid (w the neeeded Y_lm and alphas)

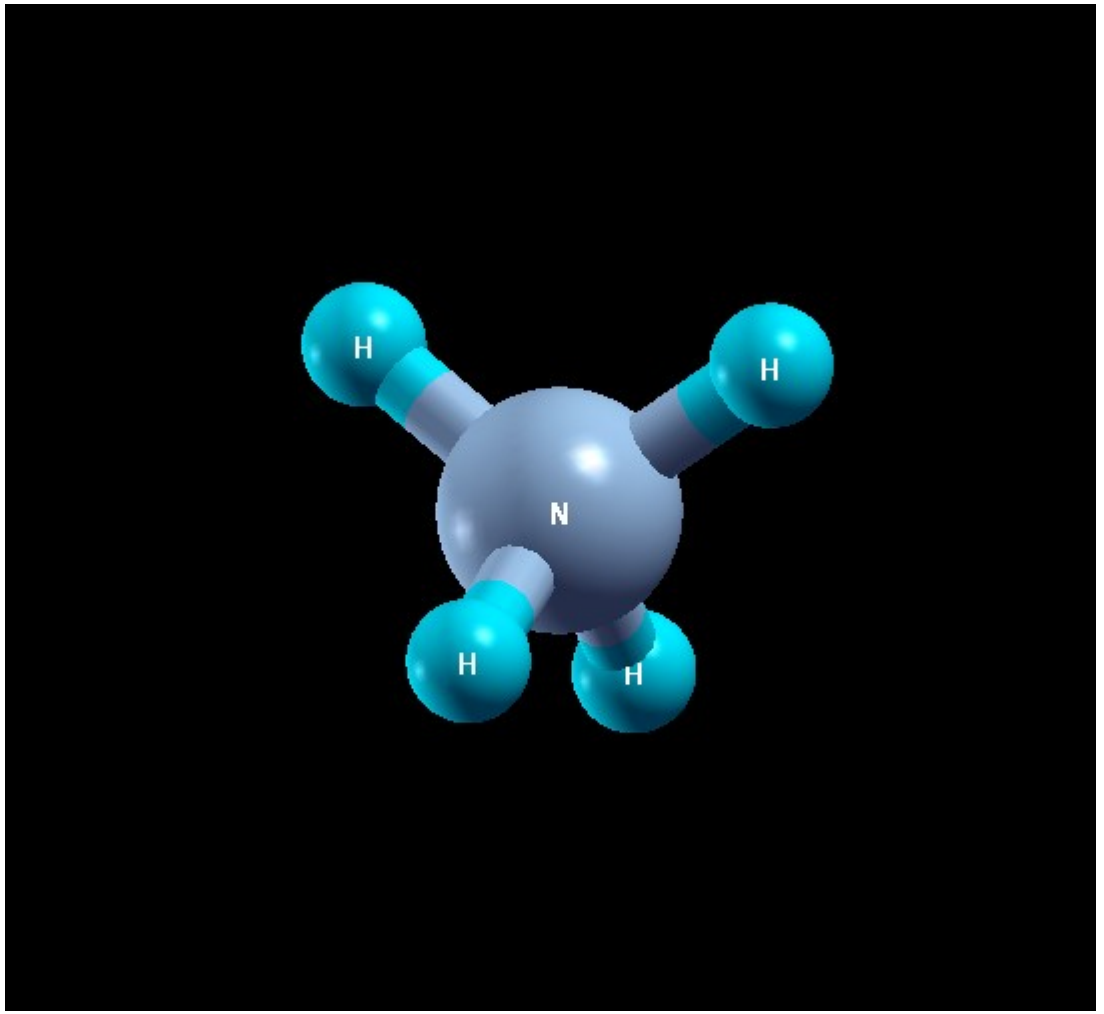
Whenever needed integrals and rho updates are performed only over the points of the above grids (addusdens_r, addusforce_r, addusstress_r, newq_r)

The betas and qs functions can be computed in reciprocal space as described above.

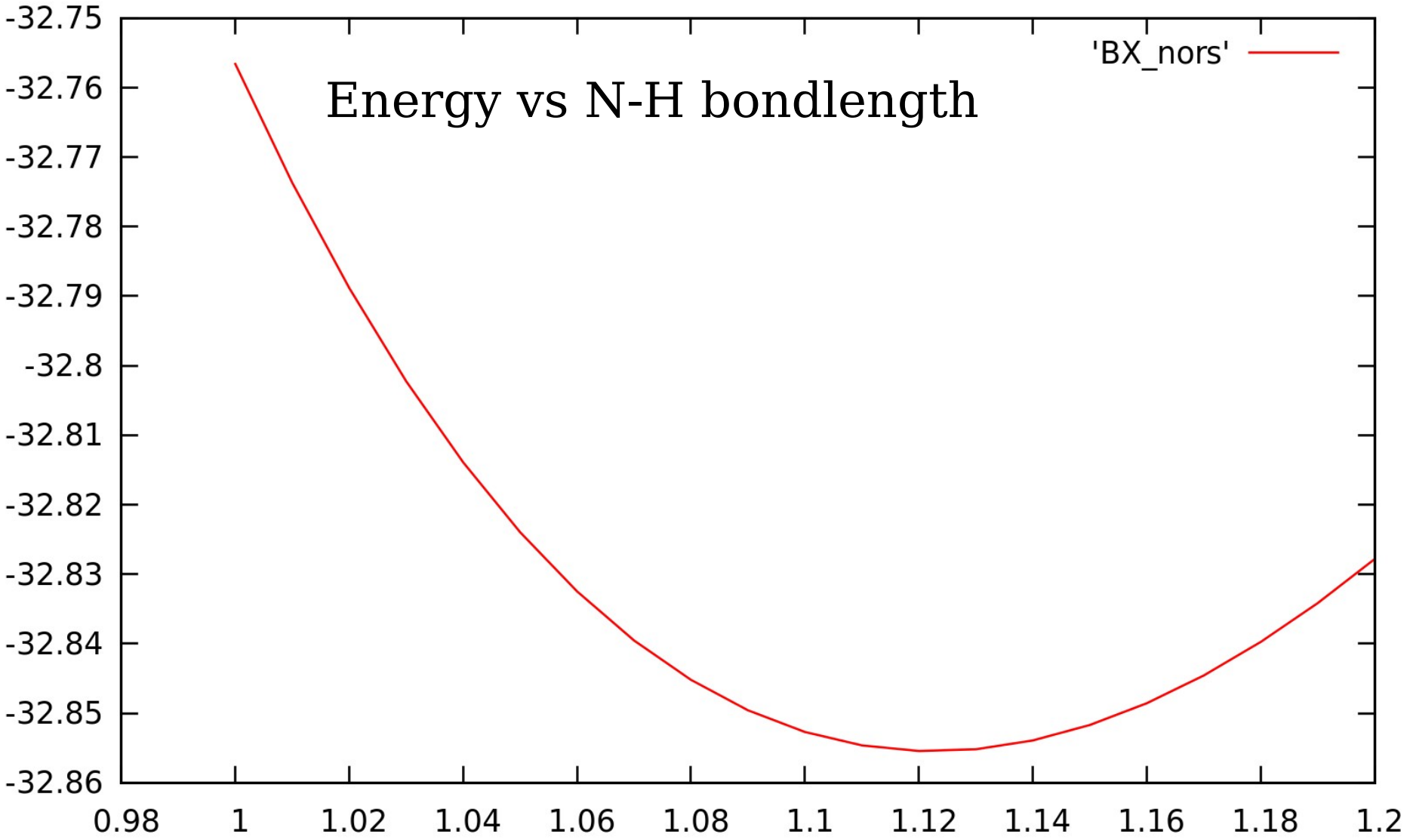
Alternatively they can be computed directly in real-space interpolating from the radial grid to the fft grid.

If the kinetic energy cutoff used is not converged enough the two procedures ARE NOT the same.

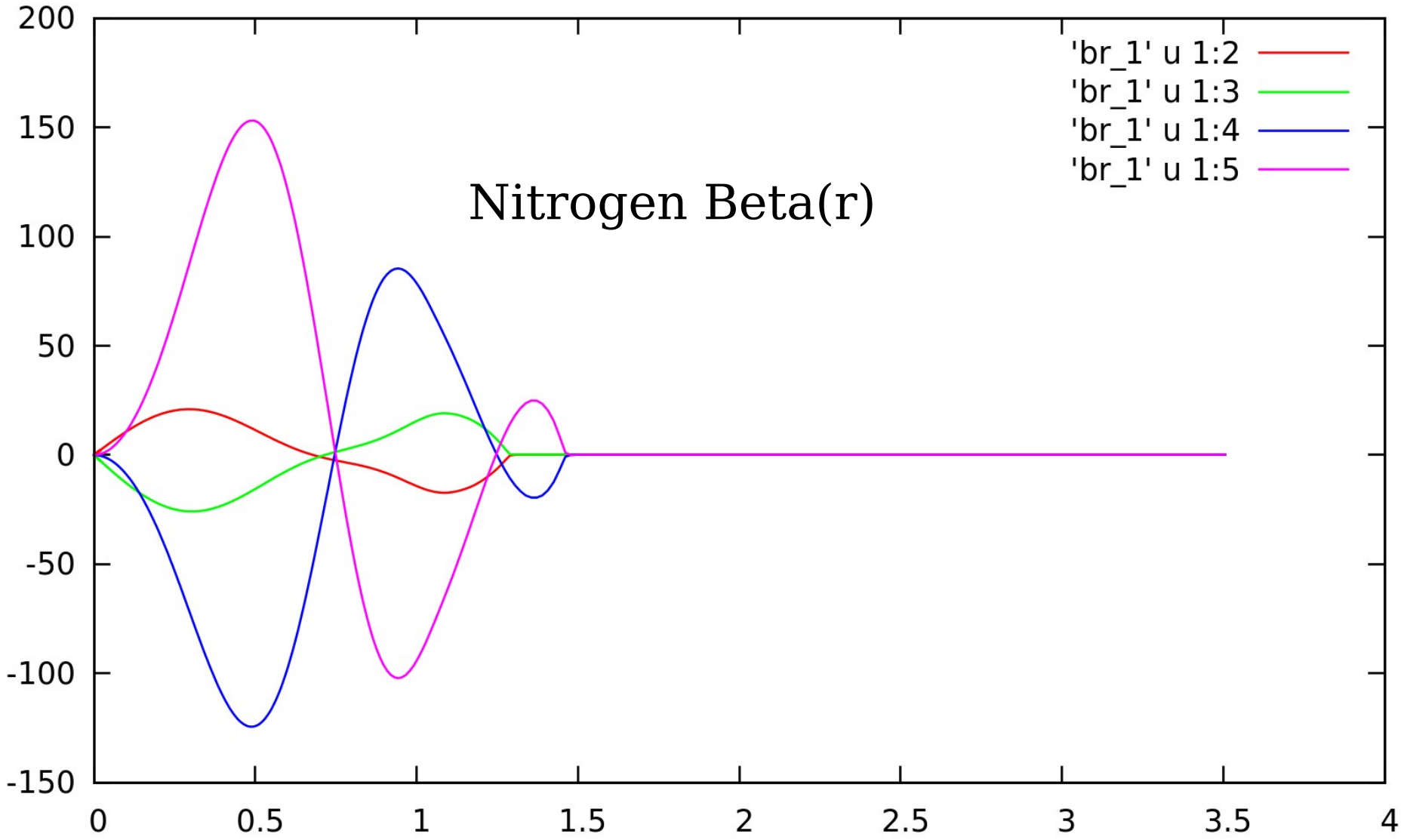
In our experience the G-space treatment has been more reliable.

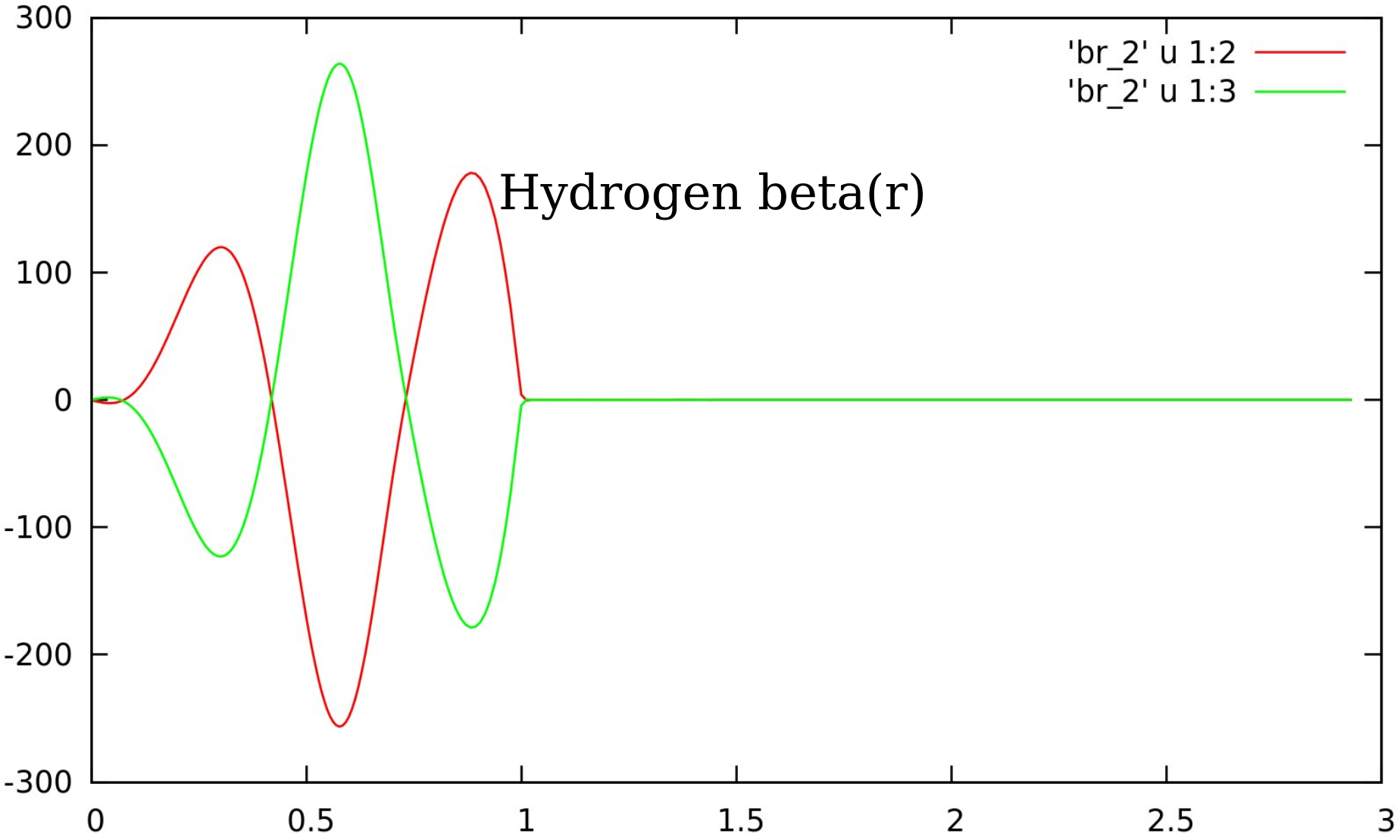


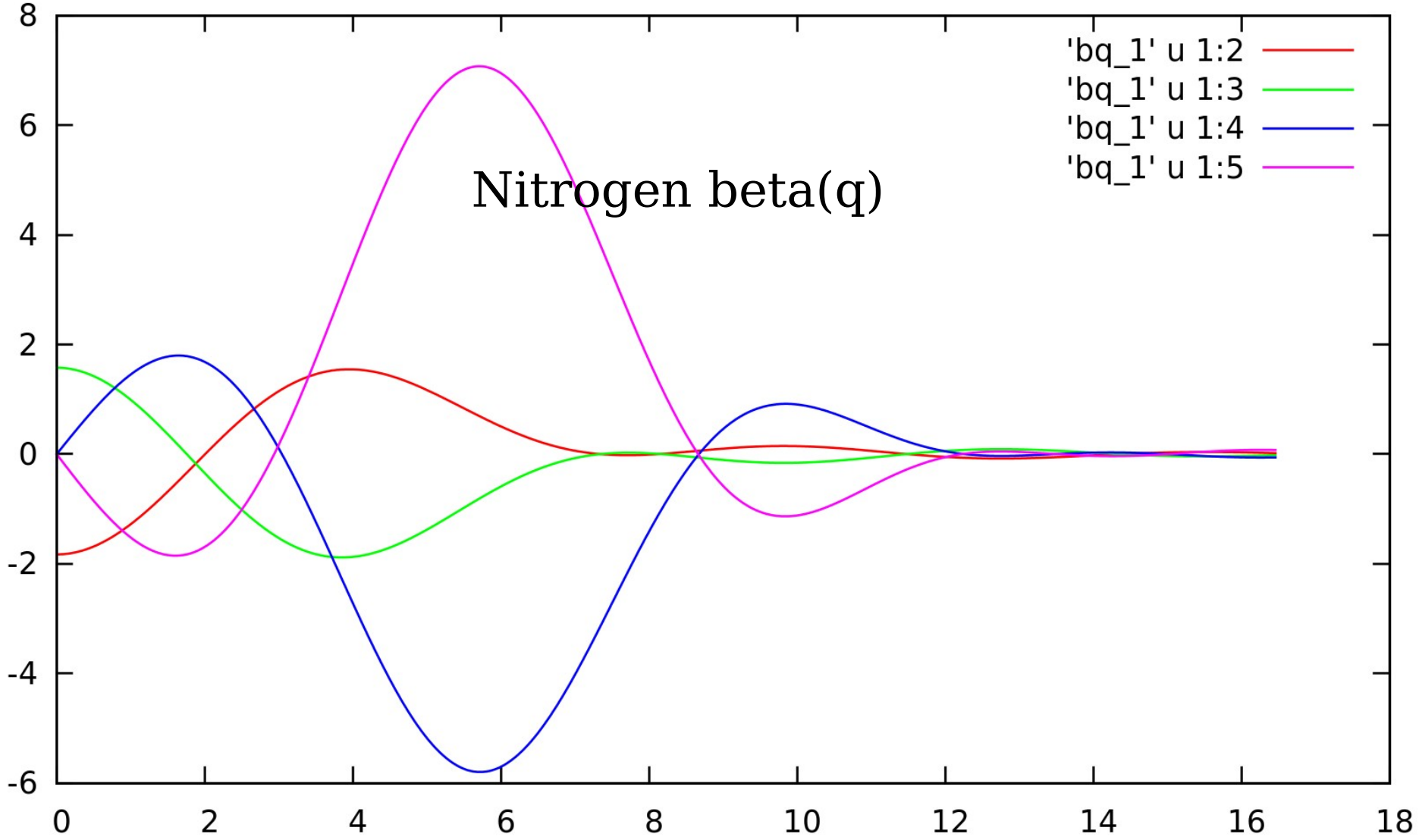
NH_4+ molecule



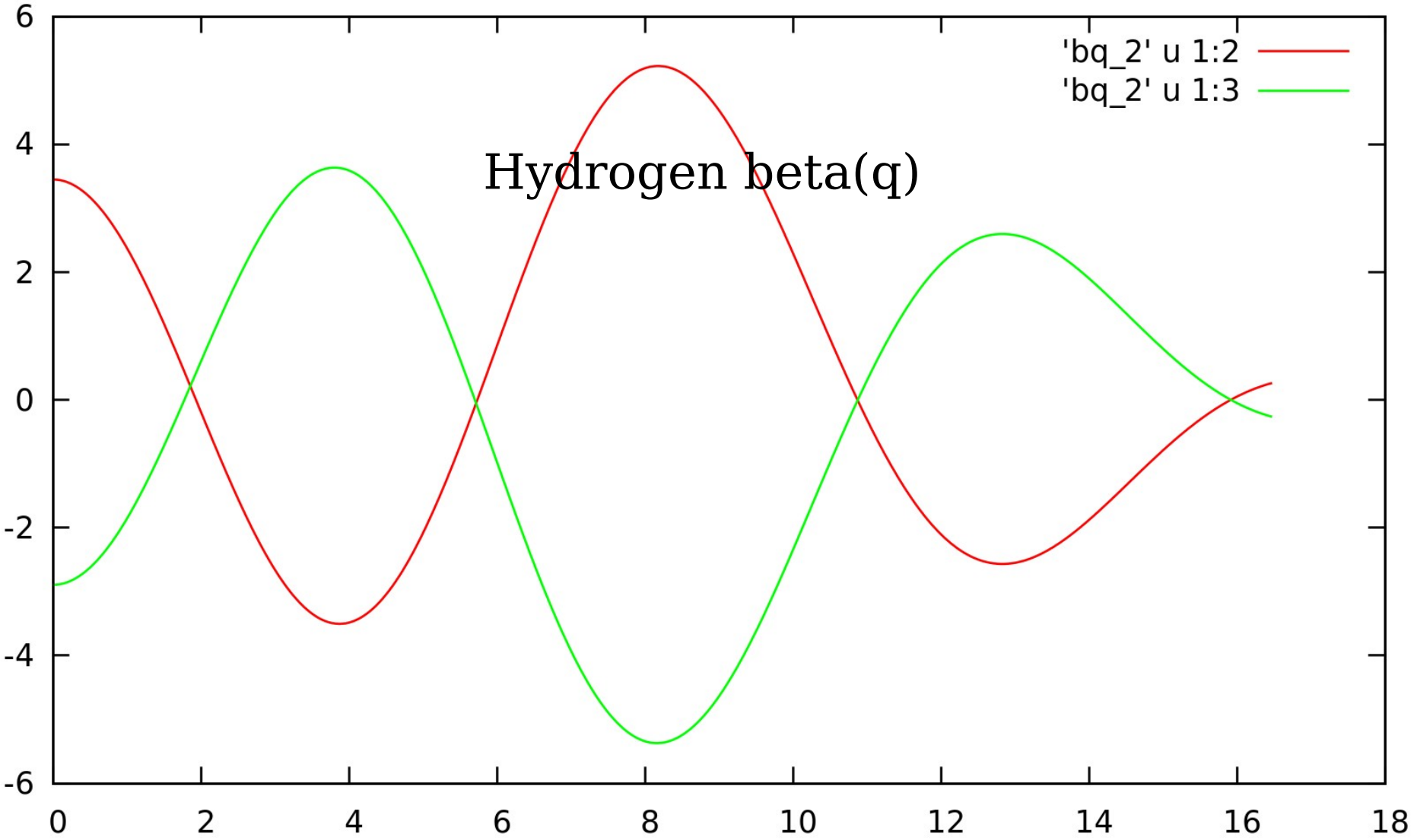
real_space=.true. CRASHES with an error due to
“S matrix not positive definite'


Nitrogen Beta(r)
'br_1' u 1:2
'br_1' u 1:3
'br_1' u 1:4
'br_1' u 1:5
200
150
100
50
0
-50
-100
-150
0
0.5
1
1.5
2
2.5
3
3.5
4


Hydrogen beta(r)
'br_2' u 1:2
'br_2' u 1:3
300
200
100
0
-100
-200
-300
0
0.5
1
1.5
2
2.5
3



Ecutwfc = 30 => qmax_wfc =sqrt(30)



Ecutwfc = 30 => qmax_wfc =sqrt(30)

PHYSICAL REVIEW B VOLUME 44, NUMBER 23 15 DECEMBER 1991-I

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Real-space implementation of nonlocal pseudopotentials for first-principles total-energy calculations

R. D. King-Smith,* M. C. Payne, and J. S. Lin
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, England
(Received 13 May 1991)

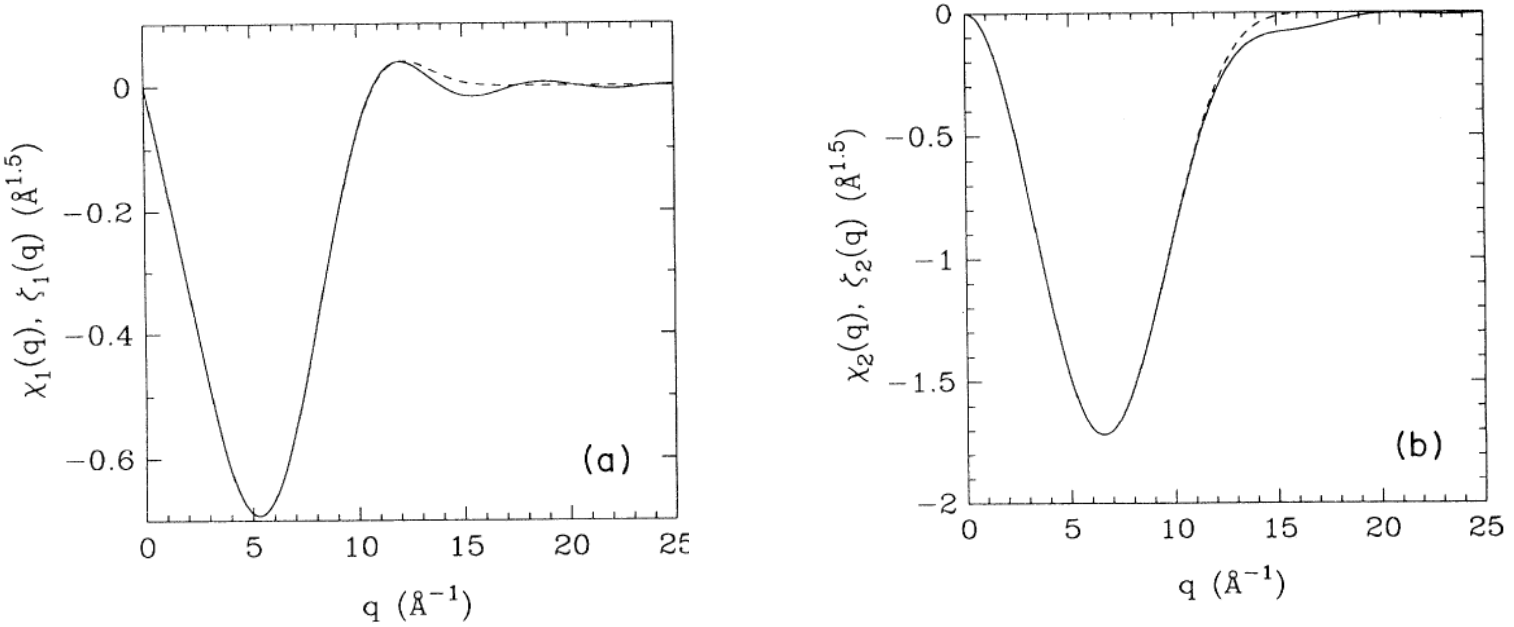


FIG. 1. (a) and (b) depict the reciprocal-space form of the $l=1$ and $l=2$ components, respectively, of the projector functions for the separable silicon potential. The solid lines show the original projectors $\zeta_l(q)$ while the dashed curves show the form of $\chi_l(q)$ derived following the prescription set out in the text.

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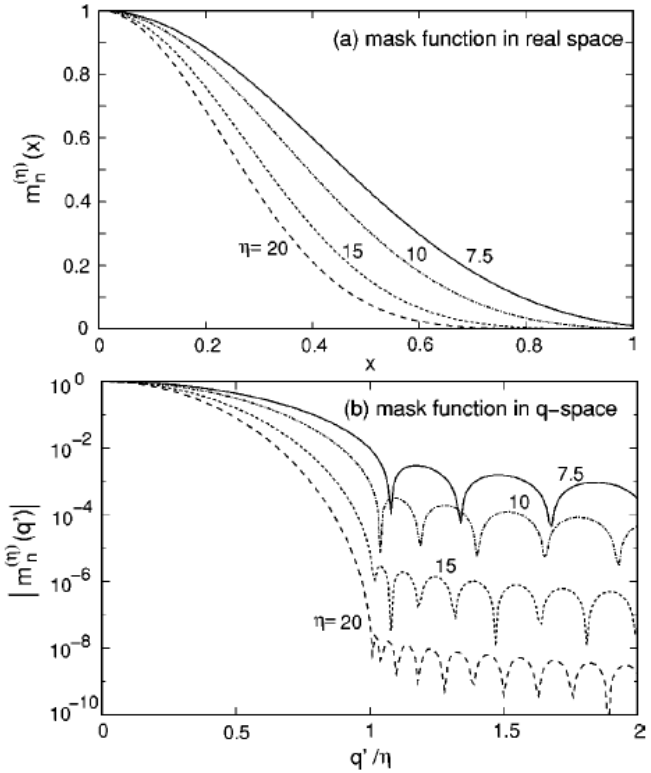
Mask-function real-space implementations of nonlocal pseudopotentials

Lin-Wang Wang
NERSC, Lawrence Berkeley National Laboratory, Berkeley, California 94720
(Received 22 August 2001; published 6 November 2001)

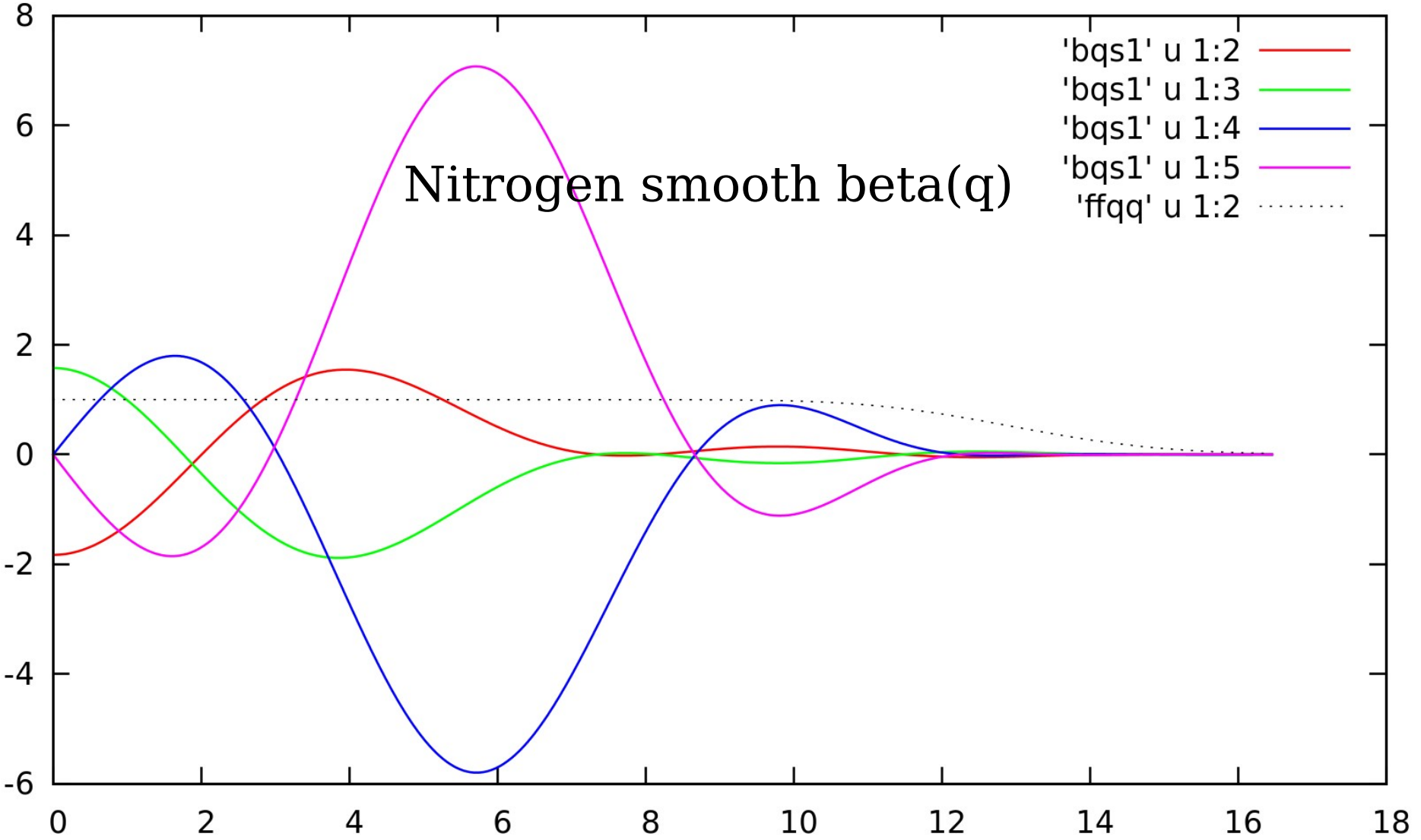
A formalism is presented for the real-space implementation of the projector based nonlocal pseudopotentials in a plane wave density functional theory calculation. A unified mask function is used to truncate the projector in real space beyond a cutoff radius. About a thousandfold improvement in the accuracy can be achieved by the use of this mask function. Compared to previous methods, the current method does not need prefitting for each individual pseudopotential.

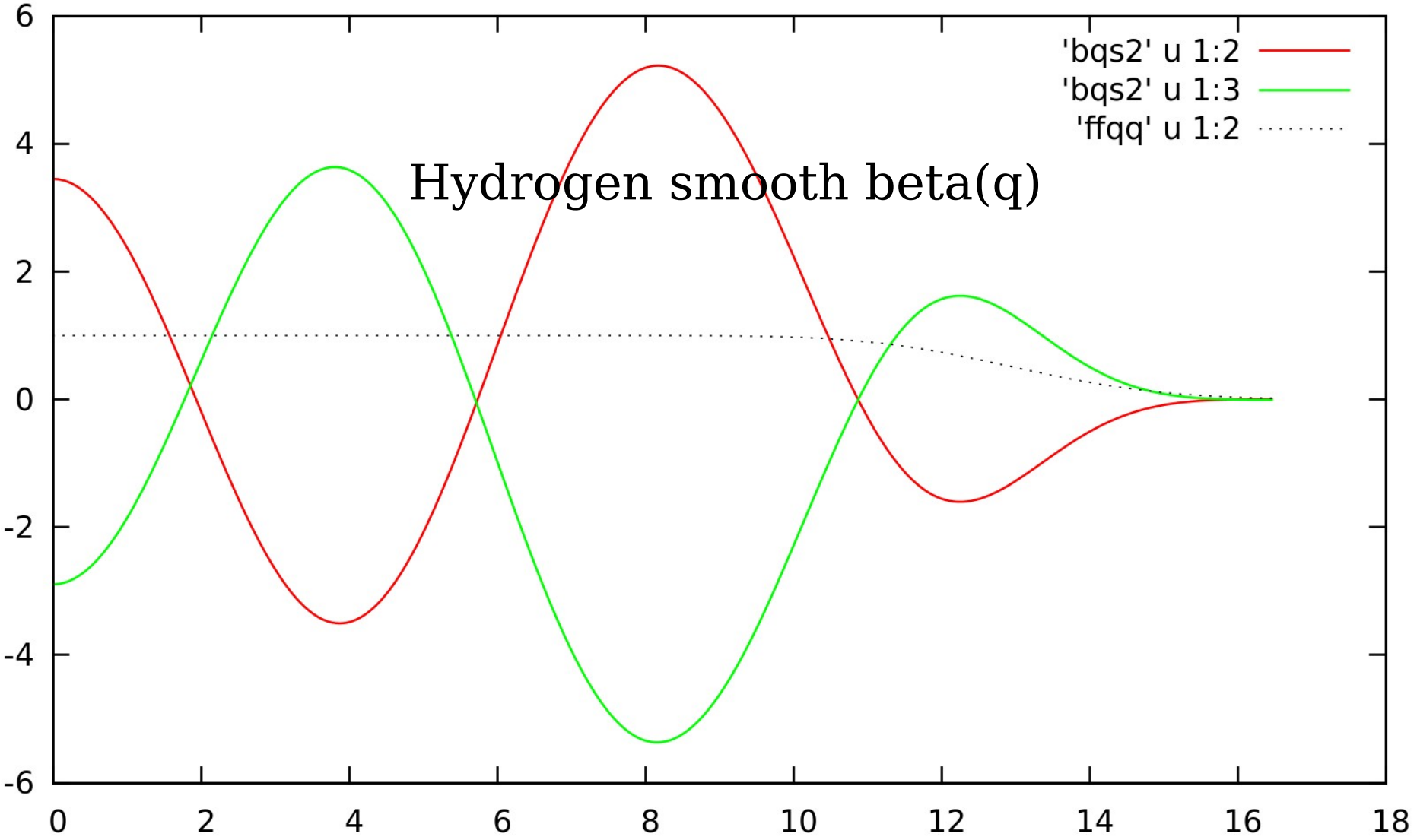
$$P=\int w(\mathbf{r})\,\frac{1}{m(r)}\,m(r)\,\psi(\mathbf{r})\,d^3r.$$

$$P=\frac{\Omega}{N}\sum_{r_i} w'_m(\mathbf{r}_i)\,m(r_i)\,\psi(\mathbf{r}_i).$$



Or just filter out the high frequency components with a function in reciprocal space that is (effectively) 1 up to qmax_wfc and decays to zero between qmax_wfc and 3 qmax_wfc.


Nitrogen smooth beta(q)
'bqs1' u 1:2
'bqs1' u 1:3
'bqs1' u 1:4
'bqs1' u 1:5
'ffqq' u 1:2
8
6
4
2
0
-2
-4
-6
0
2
4
6
8
10
12
14
16
18


Hydrogen smooth beta(q)
'bqs2' u 1:2
'bqs2' u 1:3
'ffqq' u 1:2
6
4
2
0
-2
-4
-6
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2
4
6
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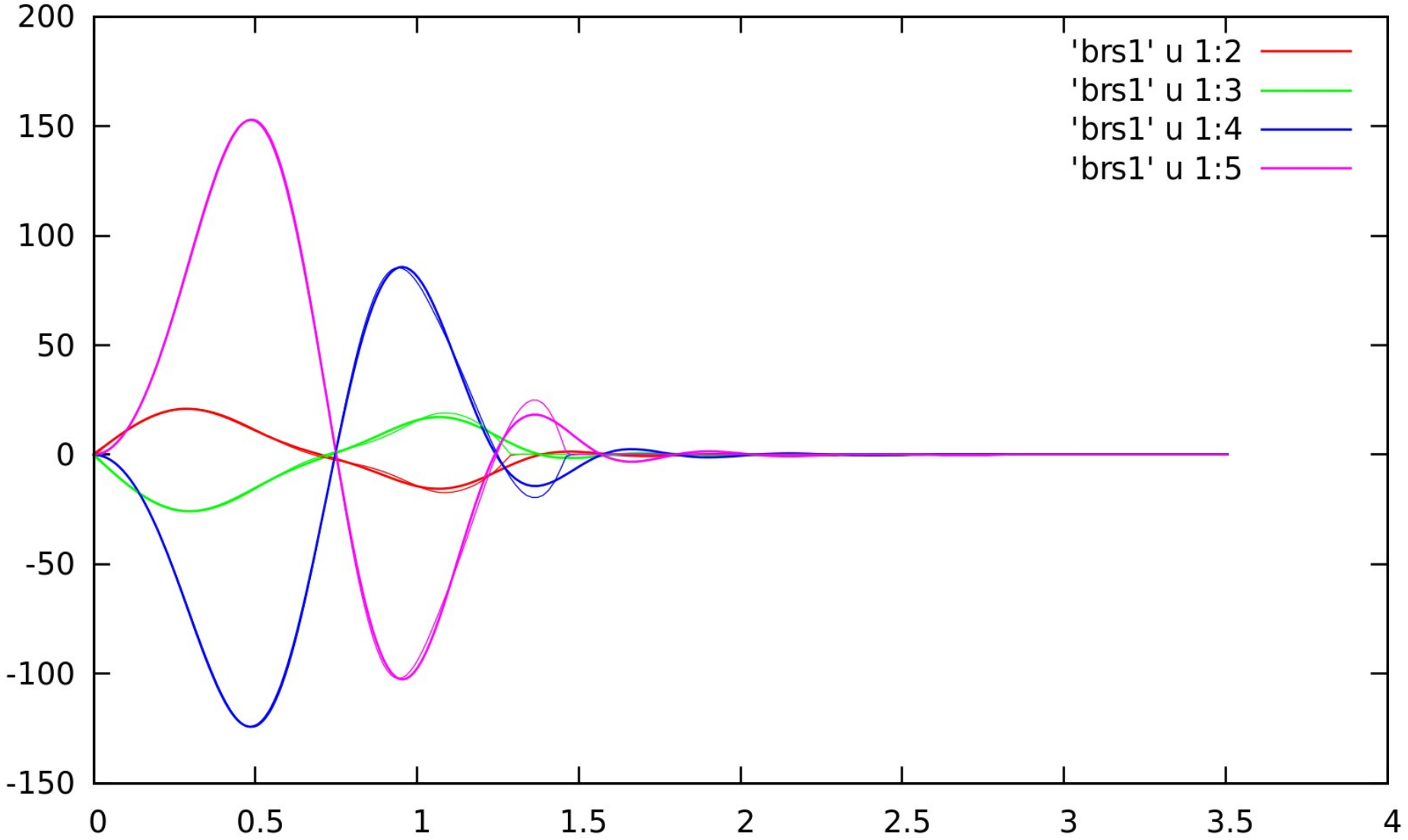
12
14
16
18


'brs1' u 1:2
'brs1' u 1:3
'brs1' u 1:4
'brs1' u 1:5
200
150
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1.5
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3
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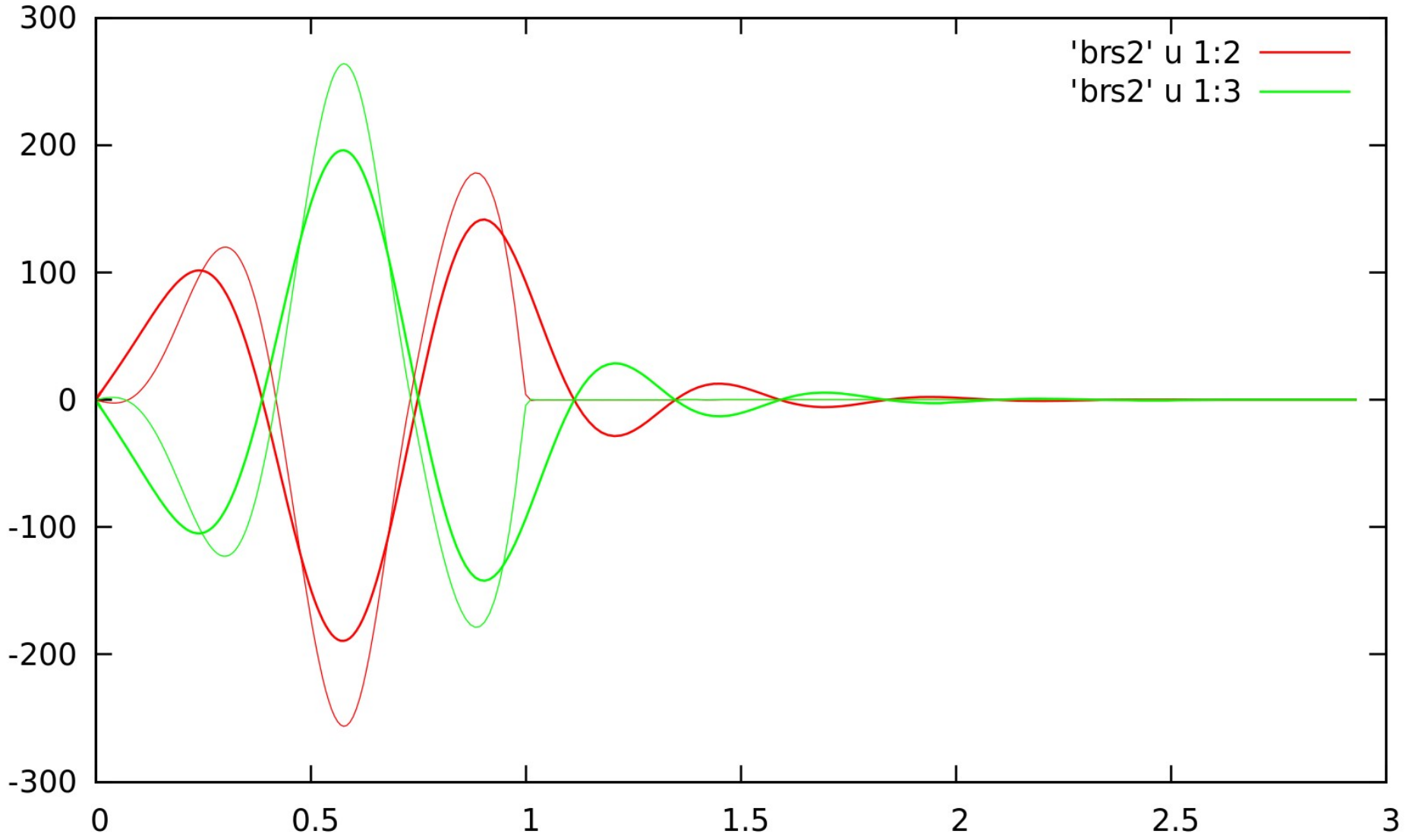
4


'brs2' u 1:2
'brs2' u 1:3
300
200
100
0
-100
-200
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0.5
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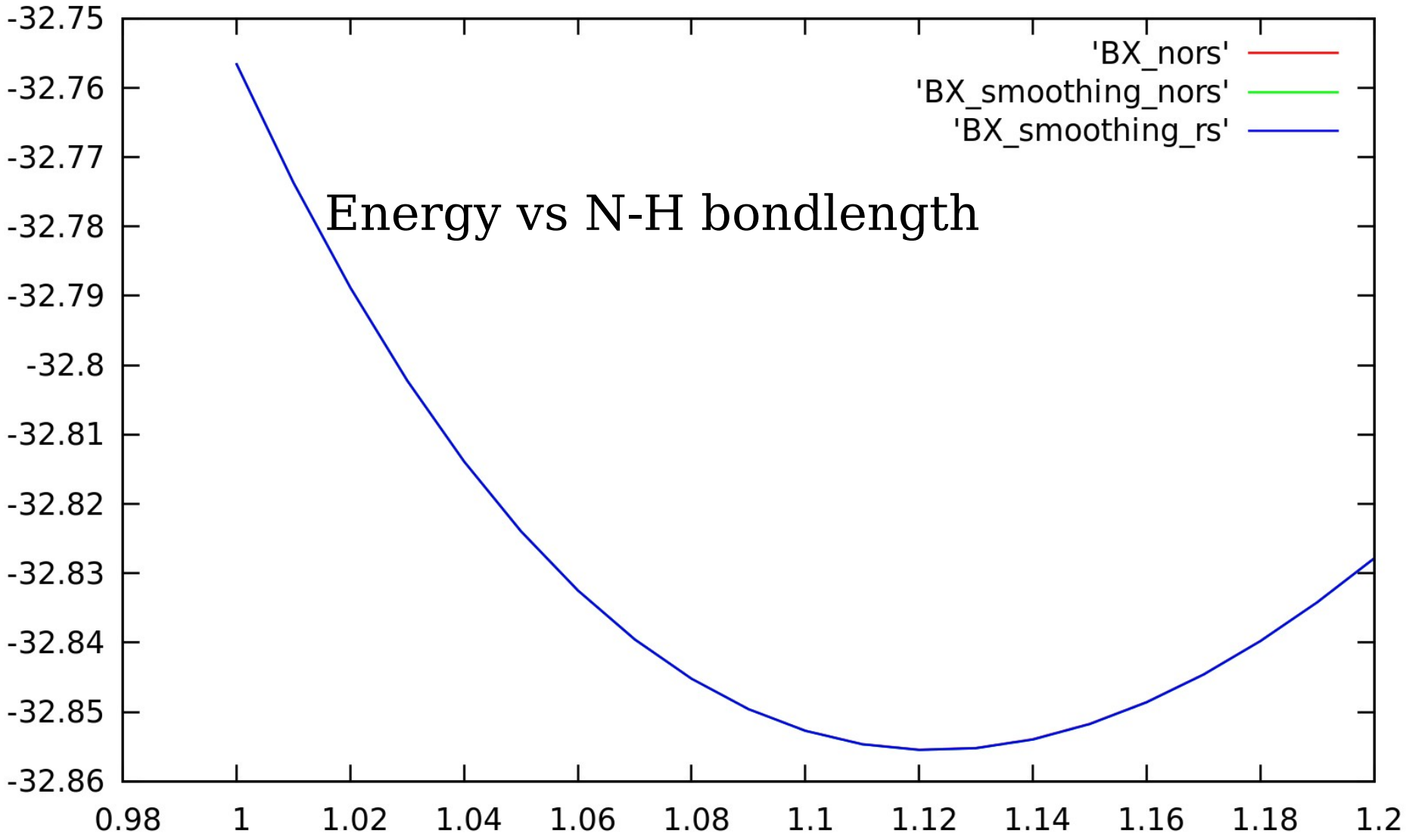
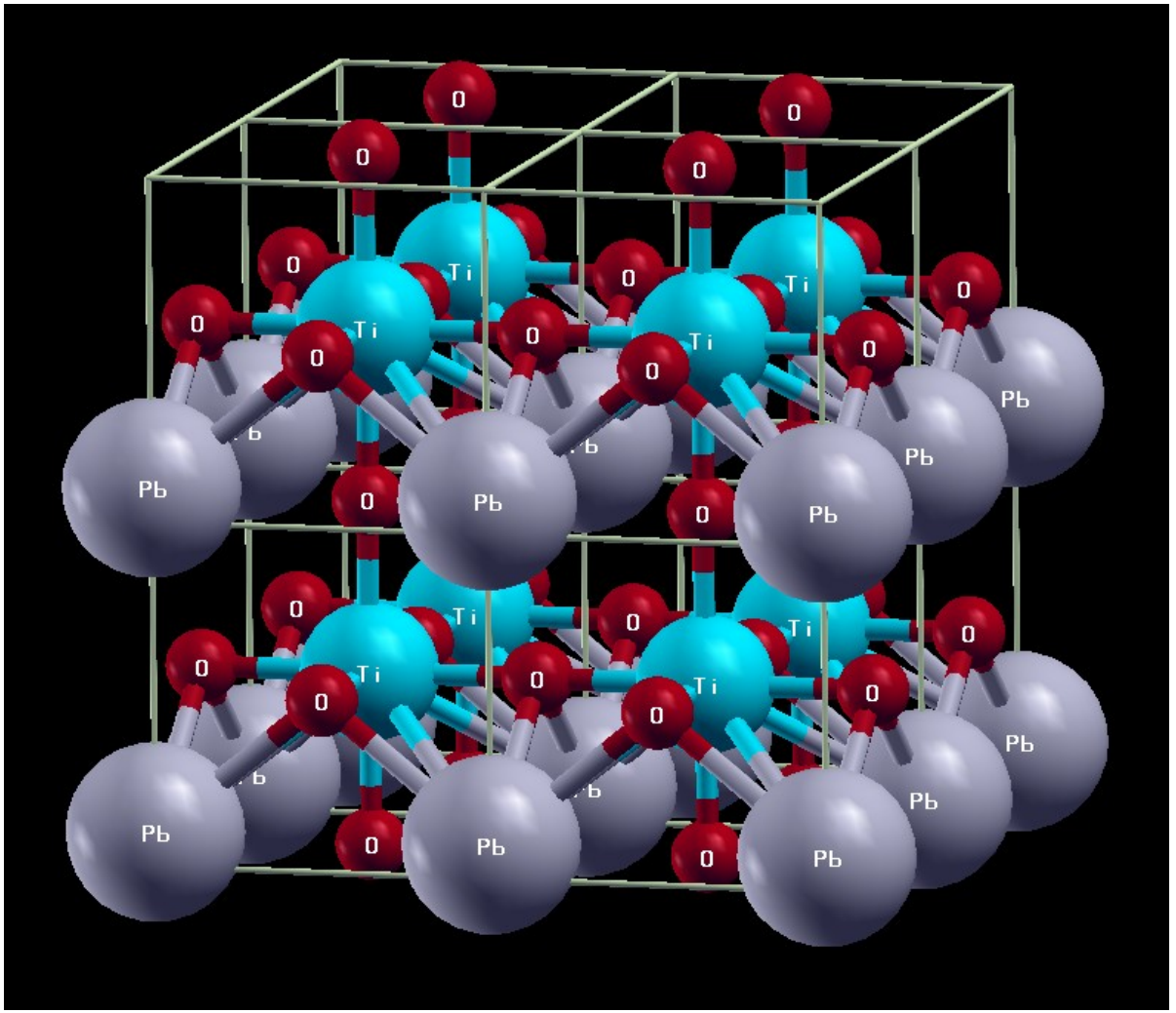
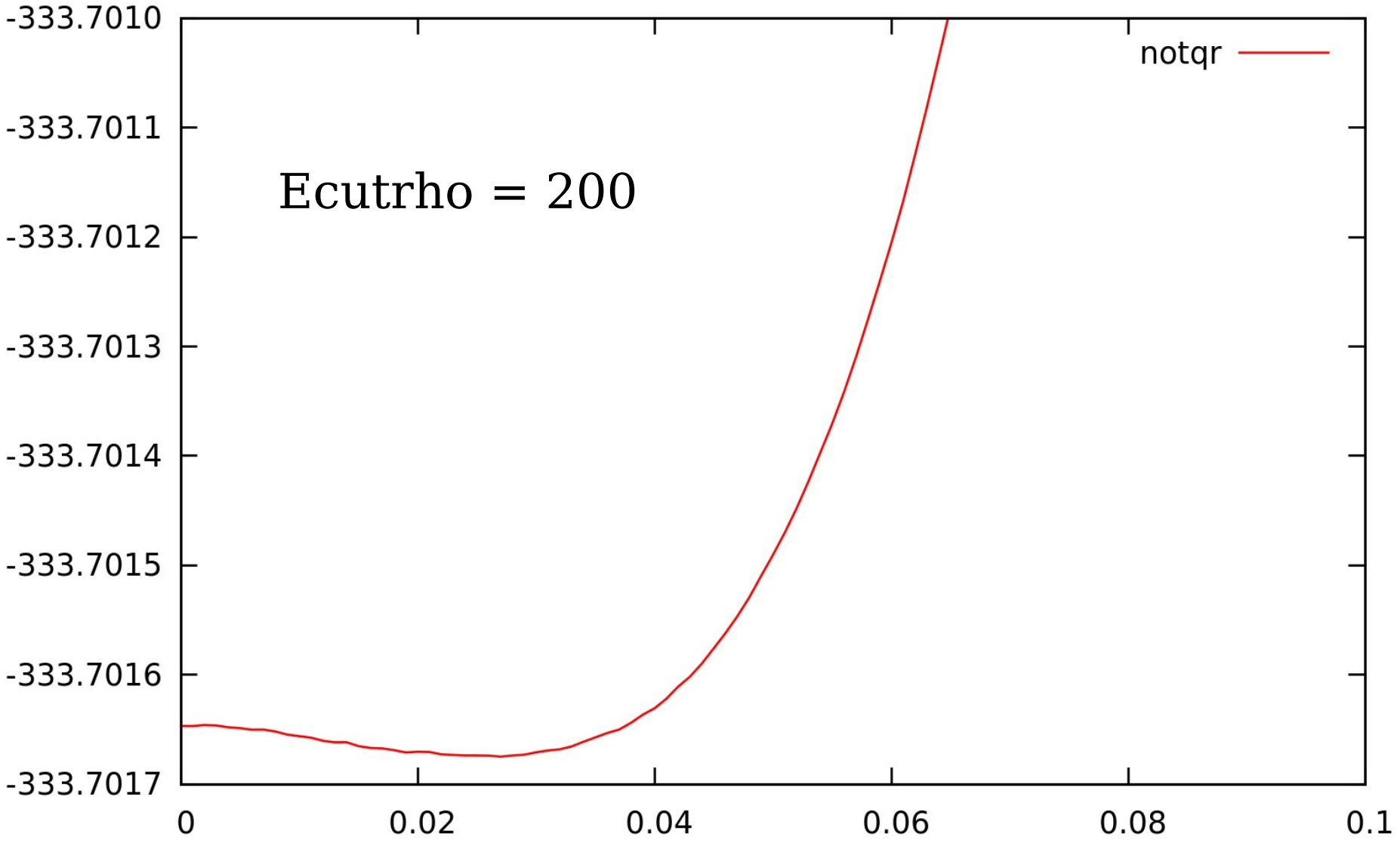


real_space=.true. w/o smoothing CRASHES with
“S matrix not positive definite'

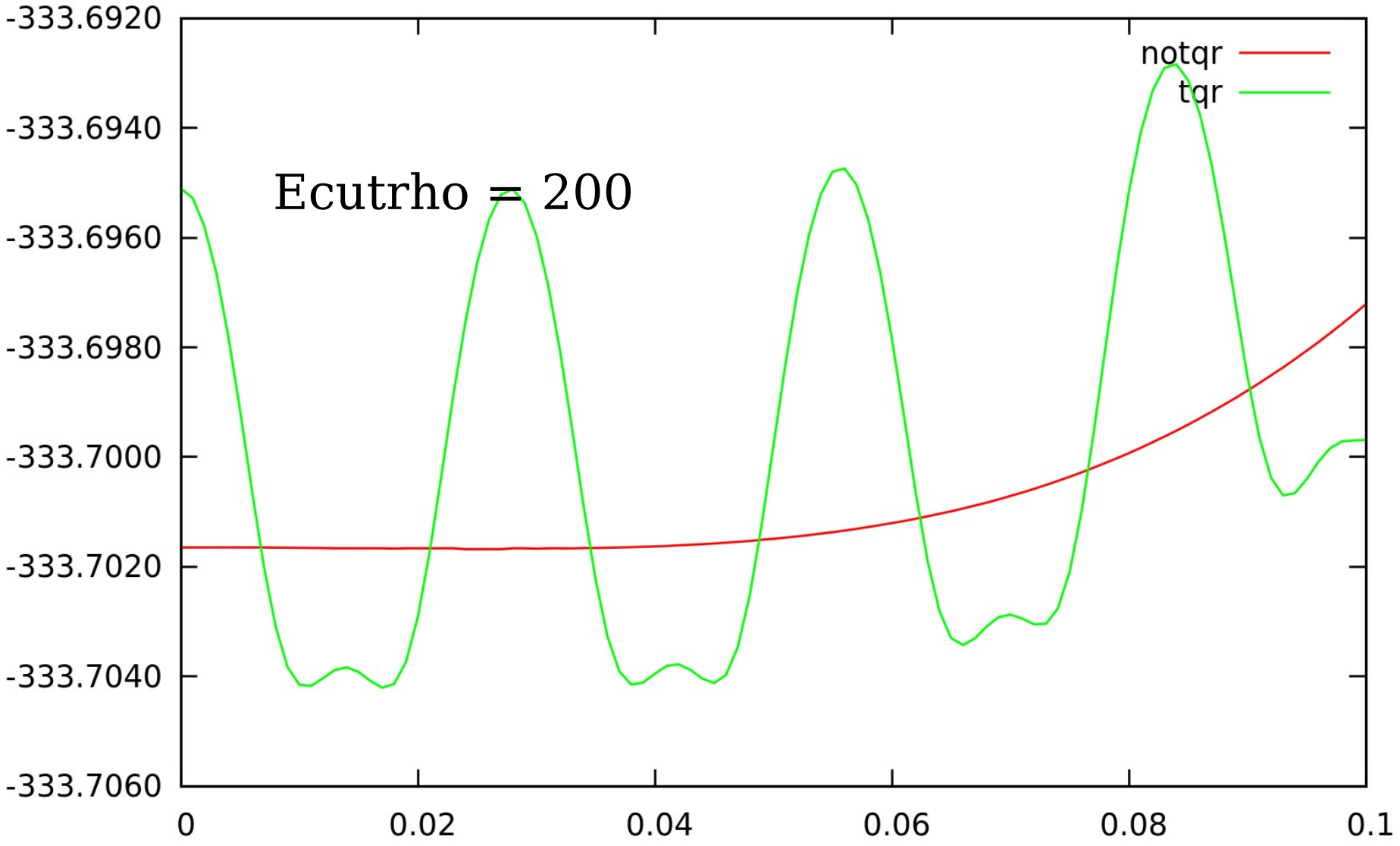


PbTiO3 perovskite

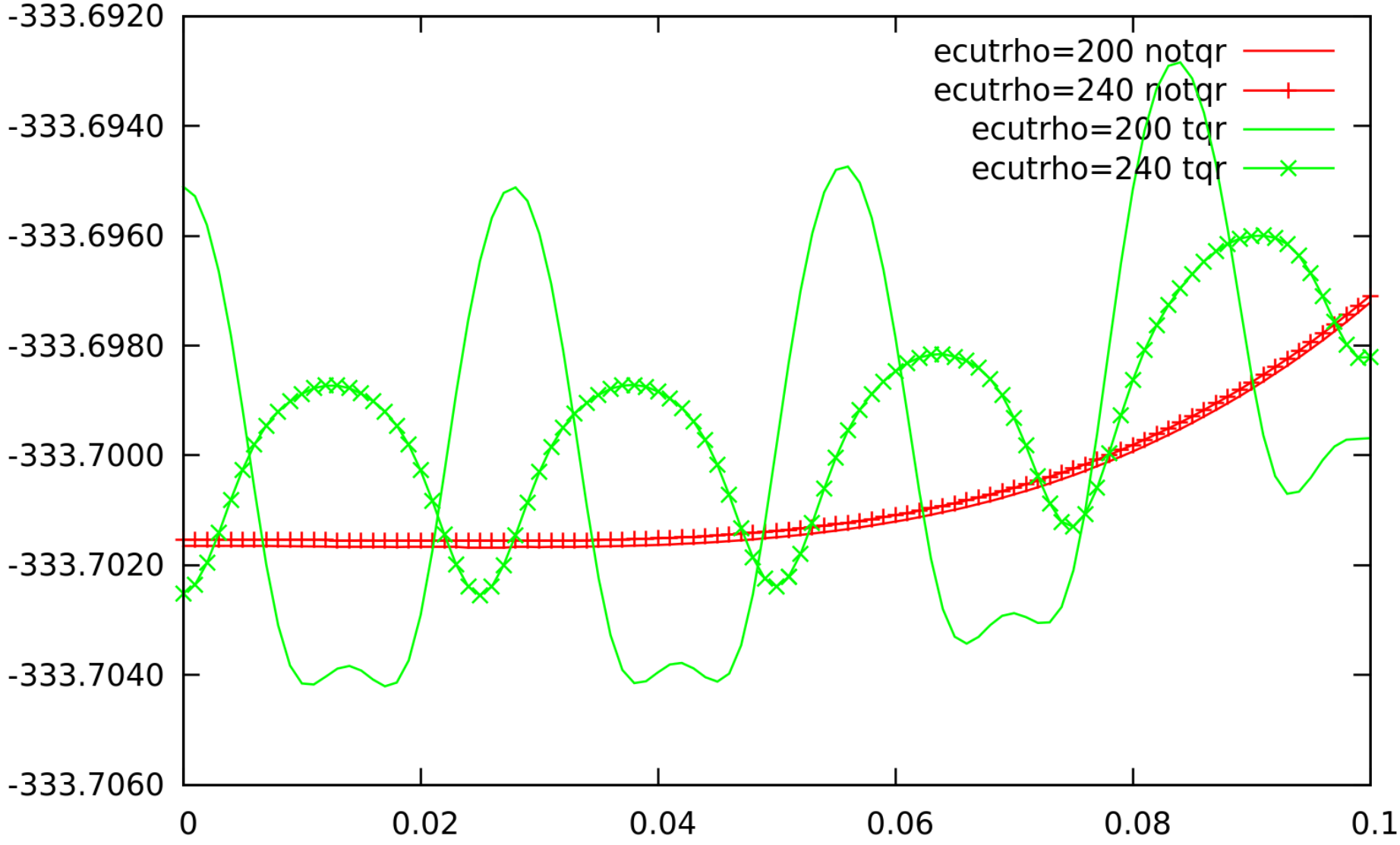
Ferroelectric instability



Energy vs ferroelectric displacement



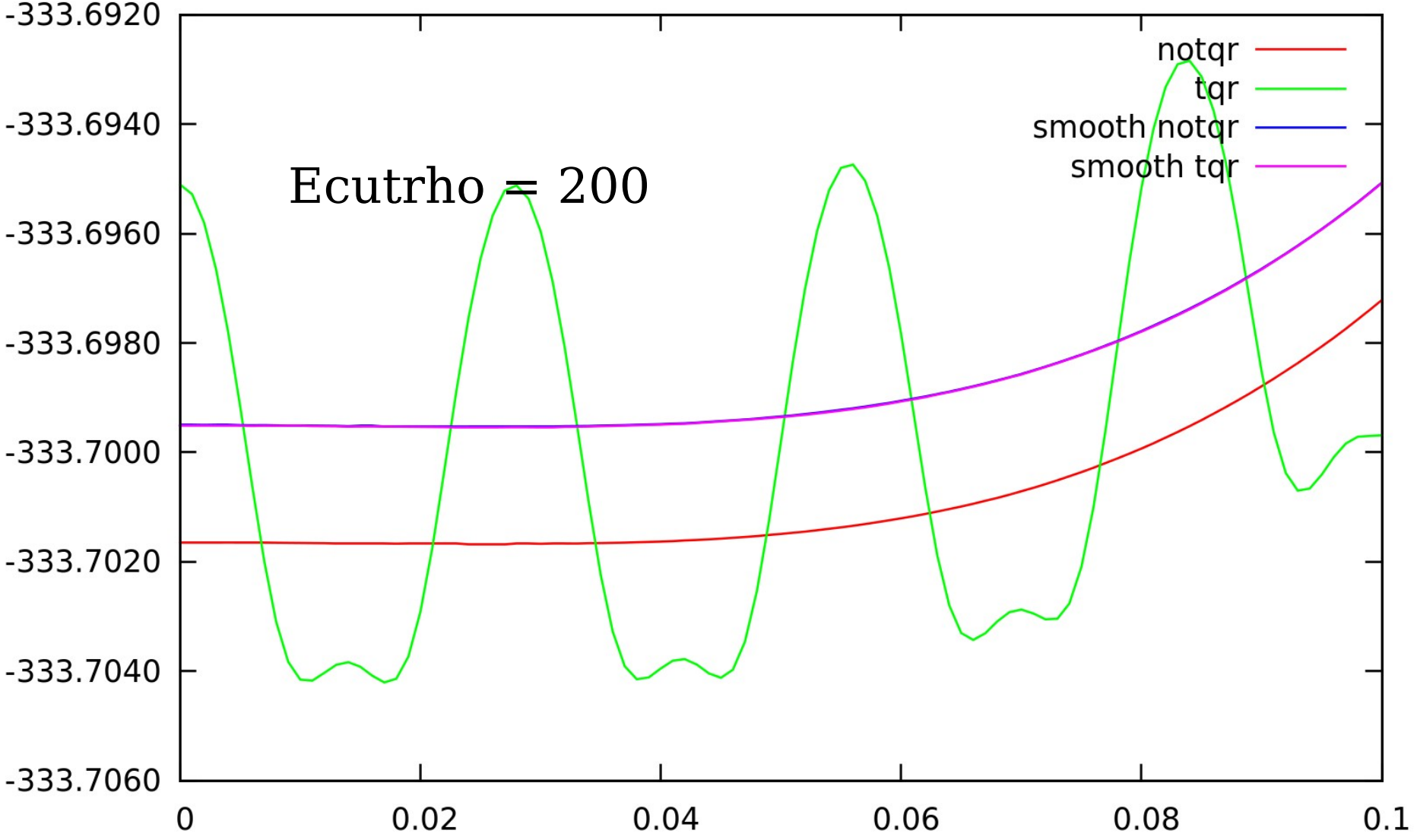
Energy vs ferroelectric displacement



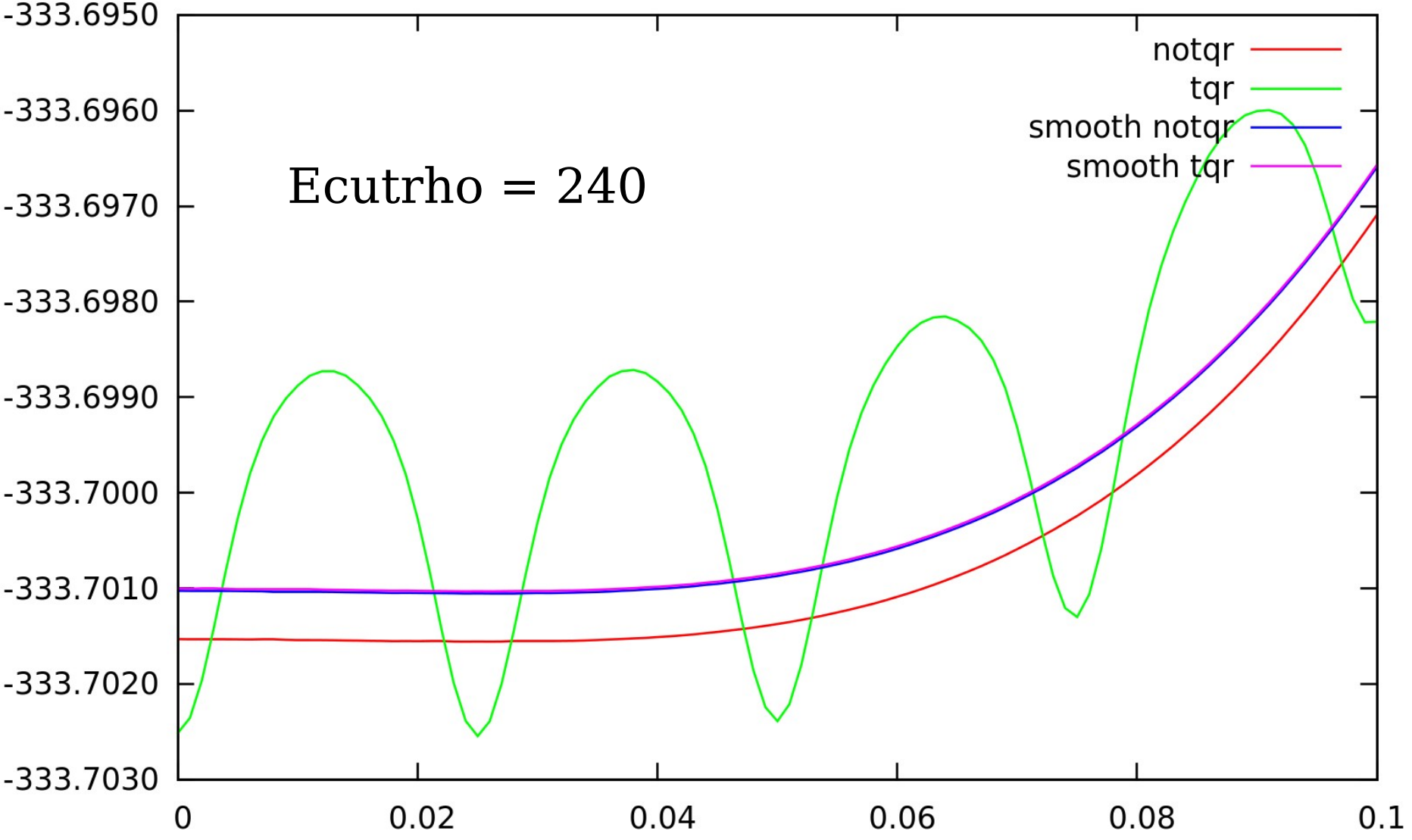
Energy vs ferroelectric displacement

We can filter the high Fourier component of the q functions and hope for the better.

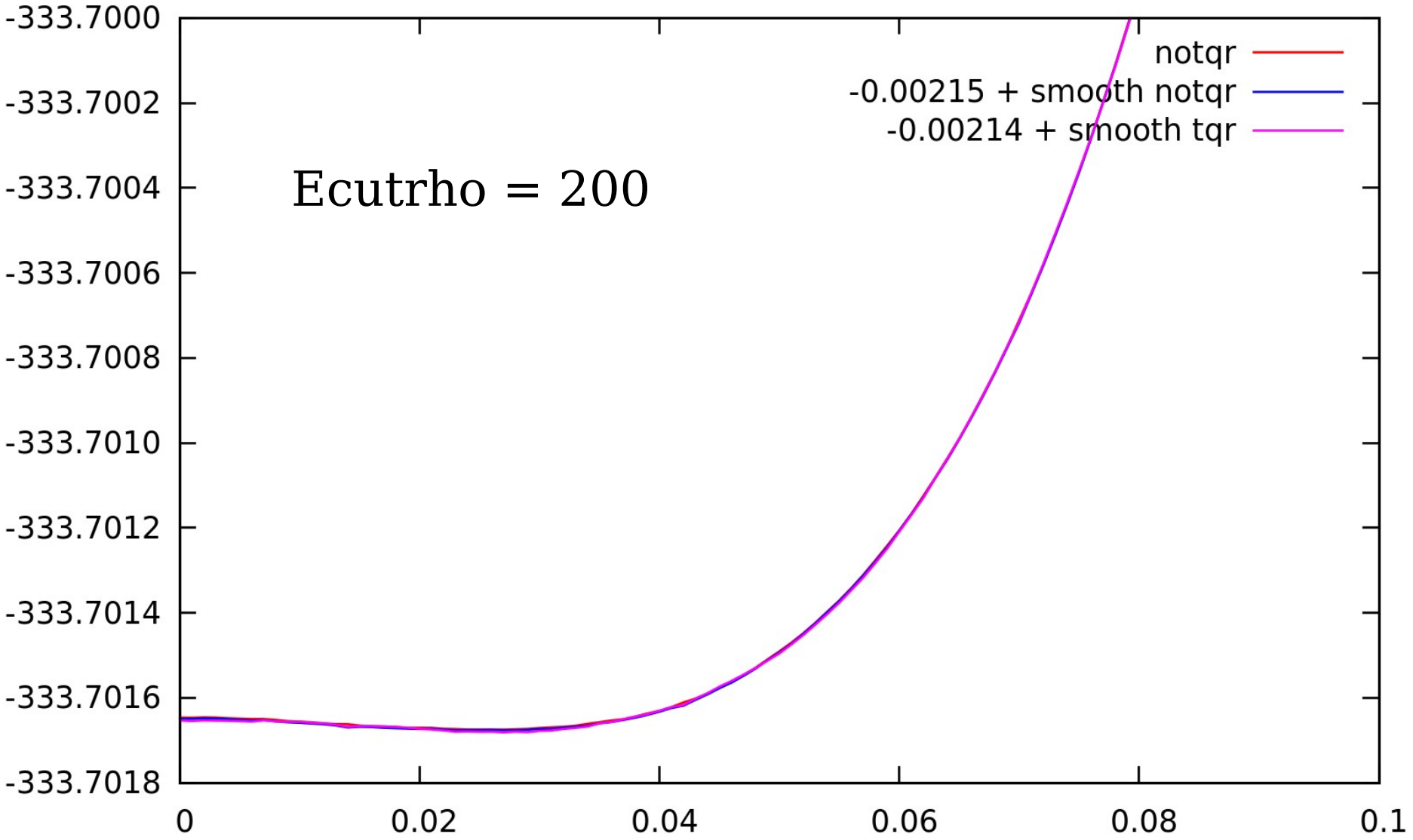
It is an additional approximation that however will vanish for ecutrho → infty so it is under control of the user.



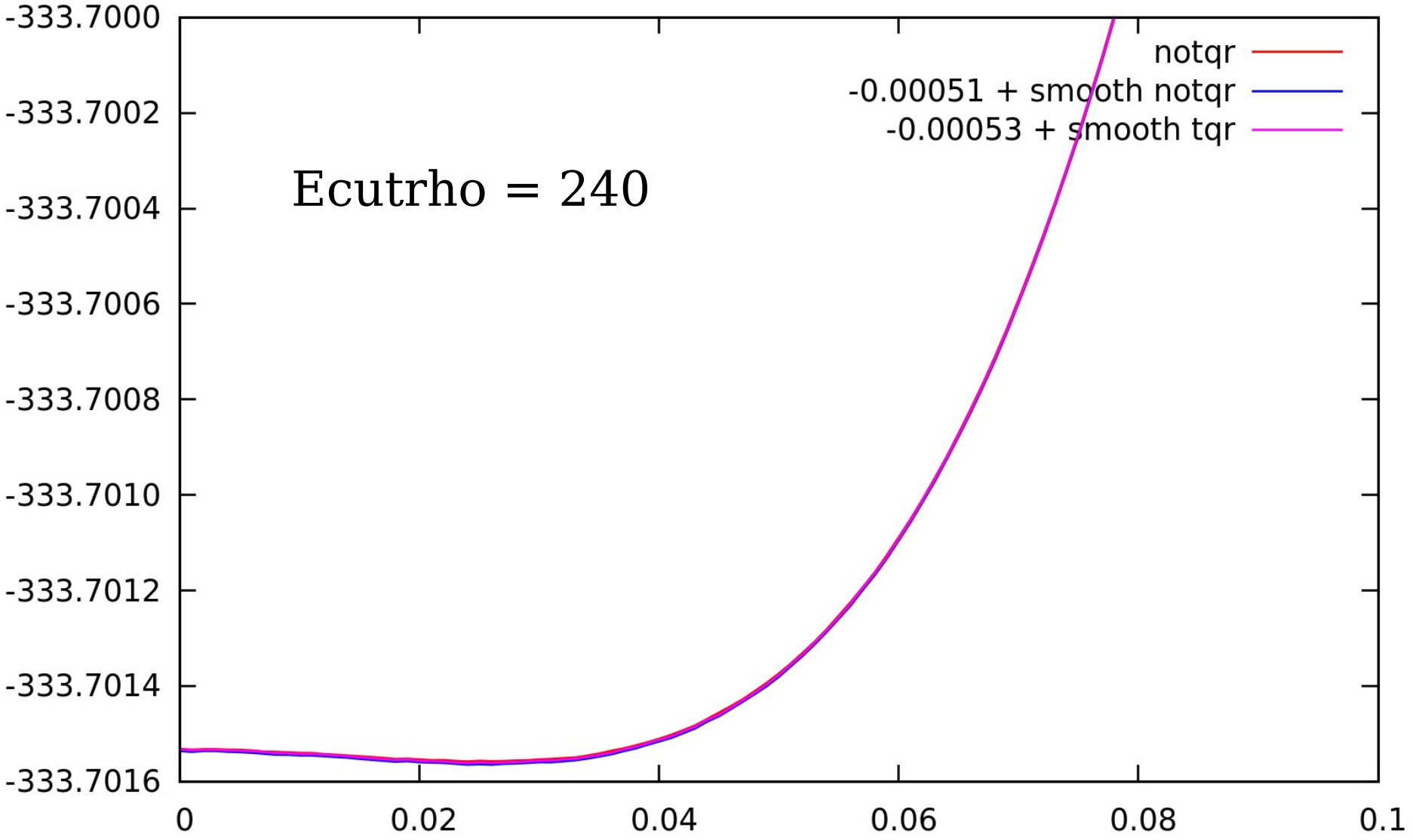
Energy vs ferroelectric displacement



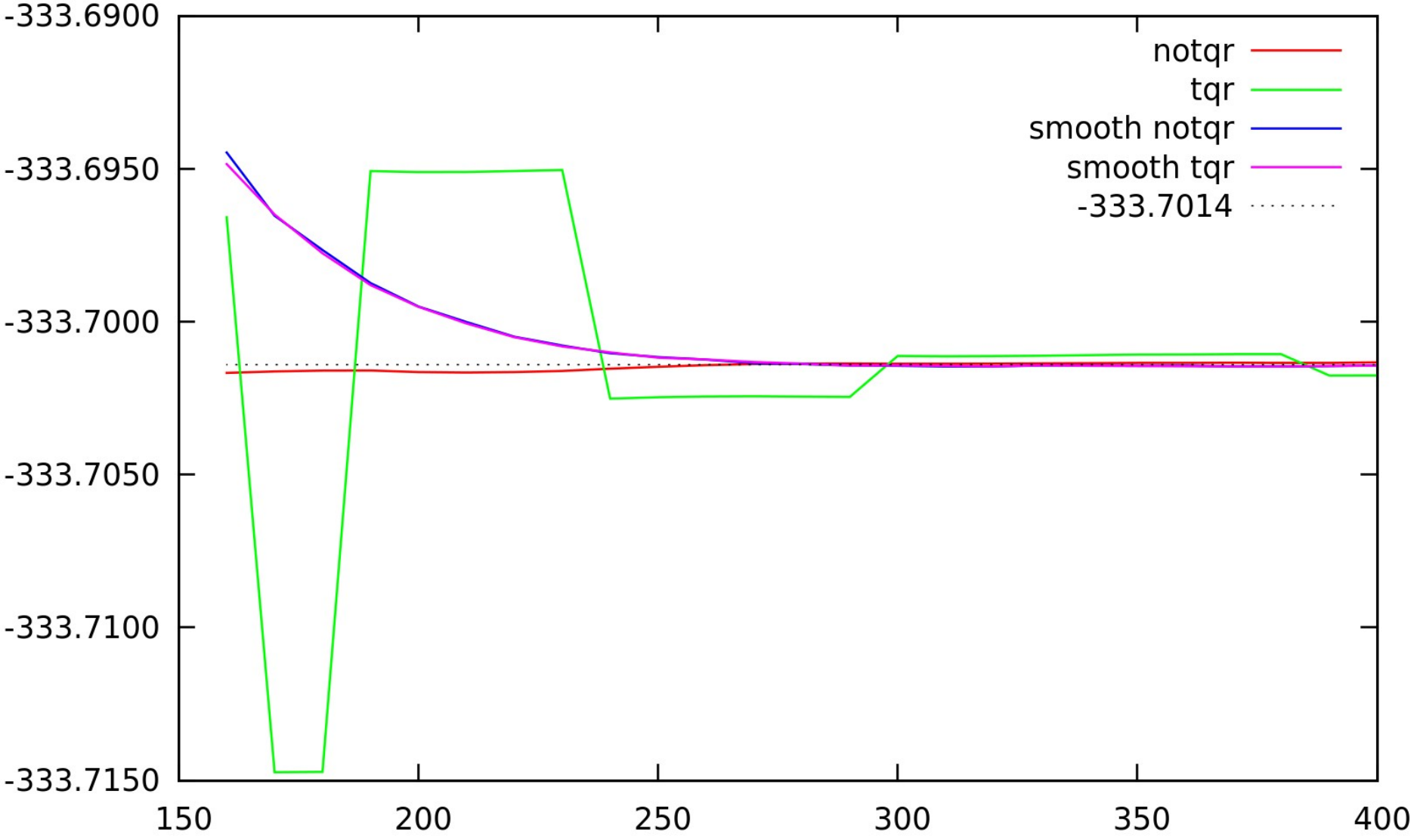
Energy vs ferroelectric displacement



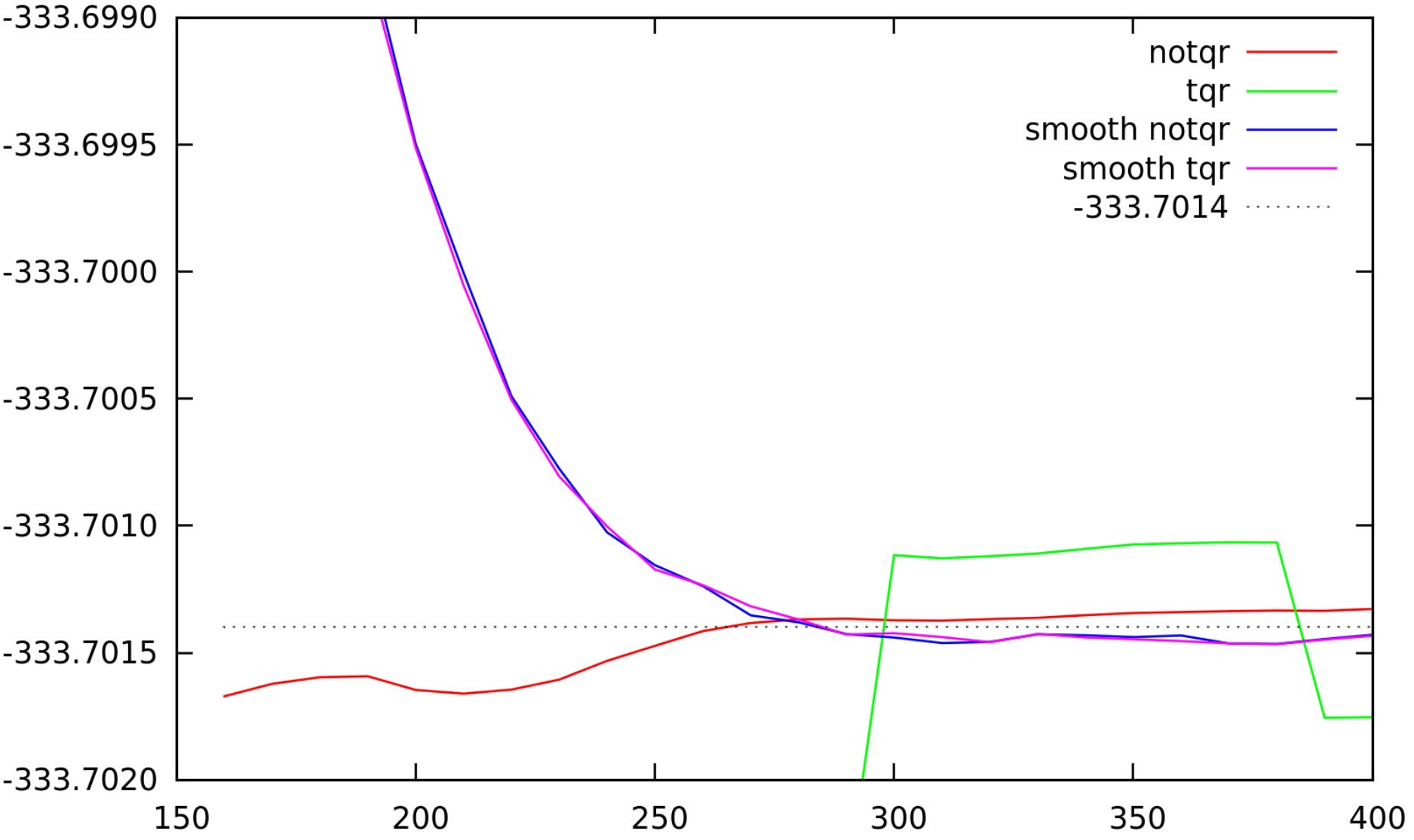
Energy vs ferroelectric displacement



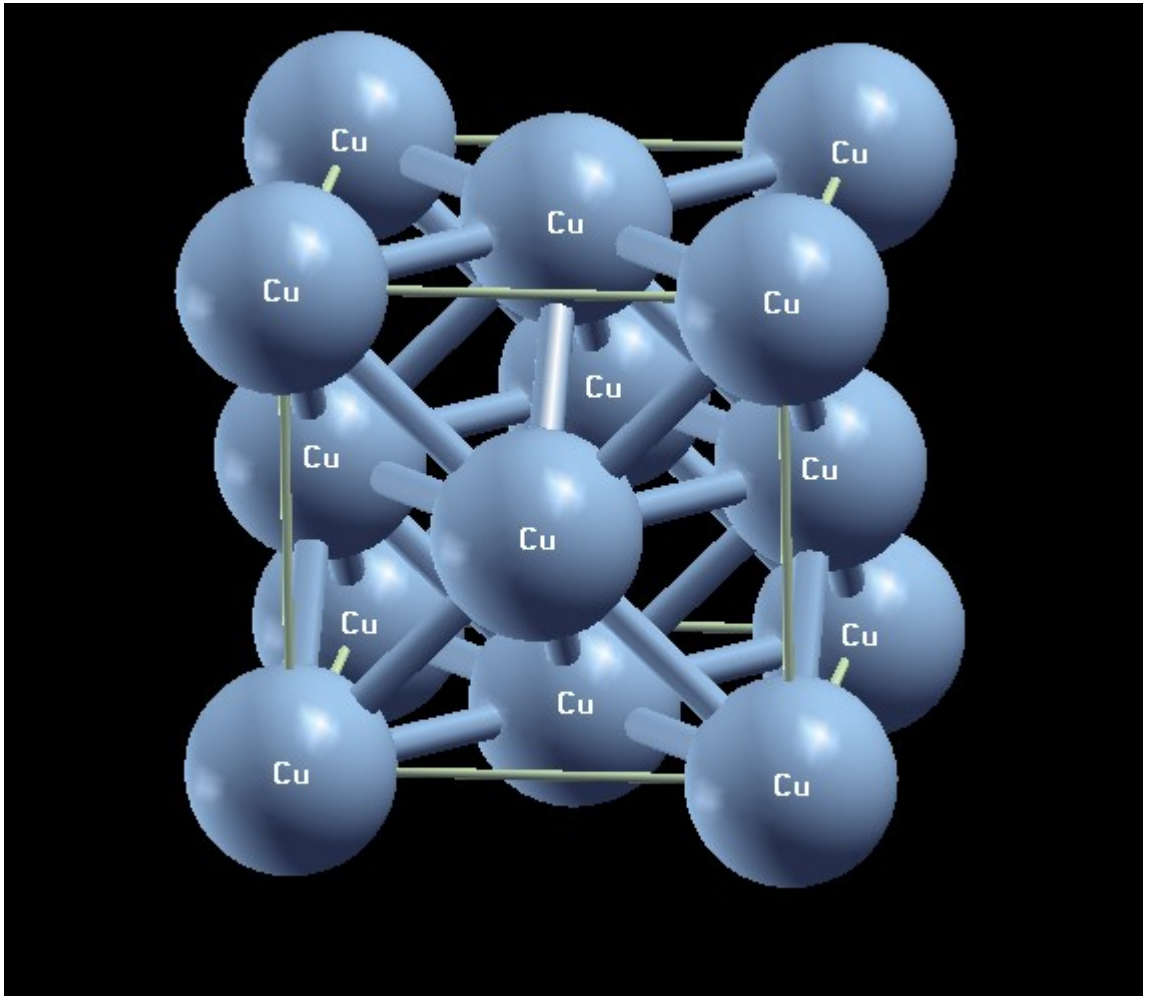
Energy vs ferroelectric displacement



Energy (u=0) vs Ecutrho



Energy (u=0) vs Ecutrho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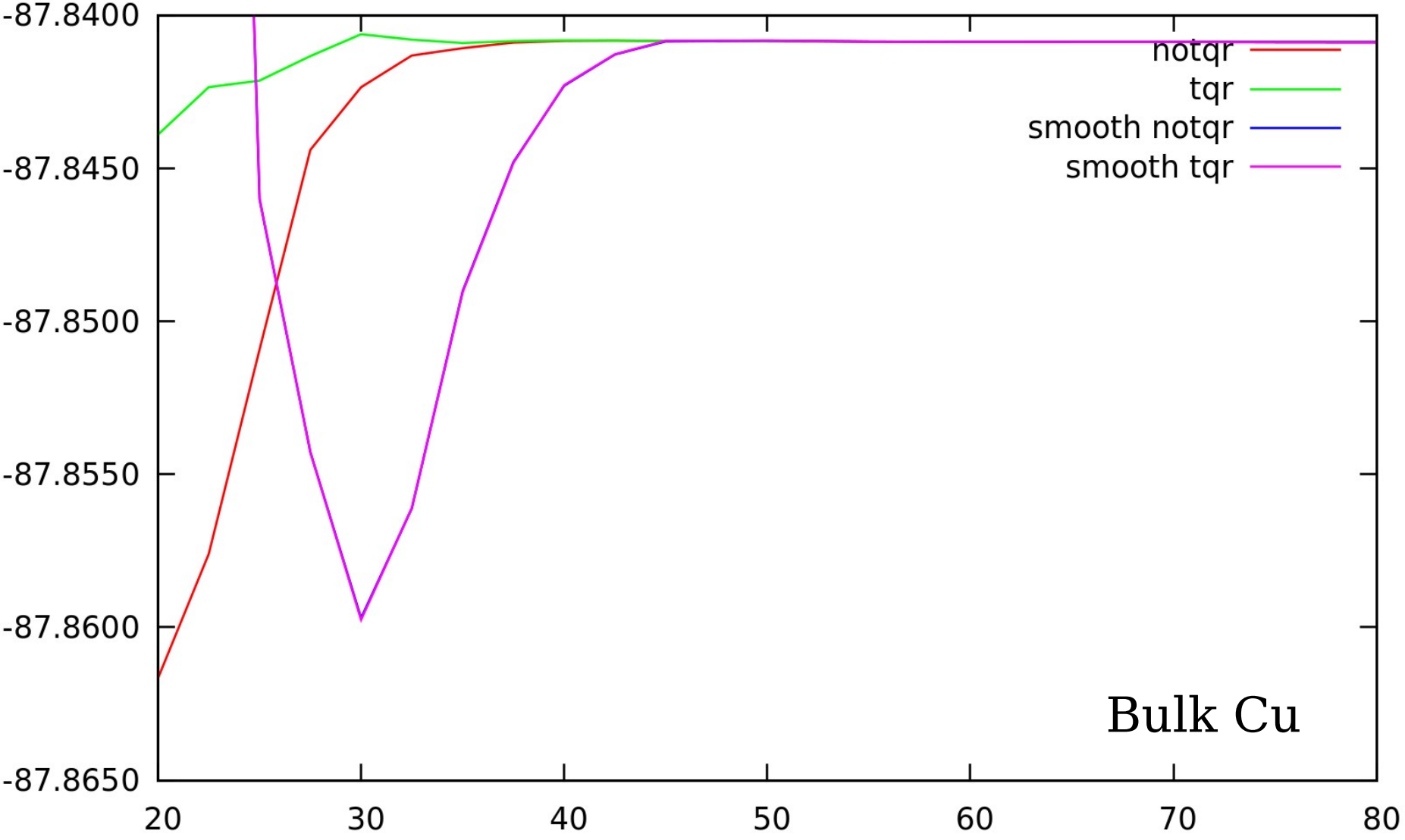
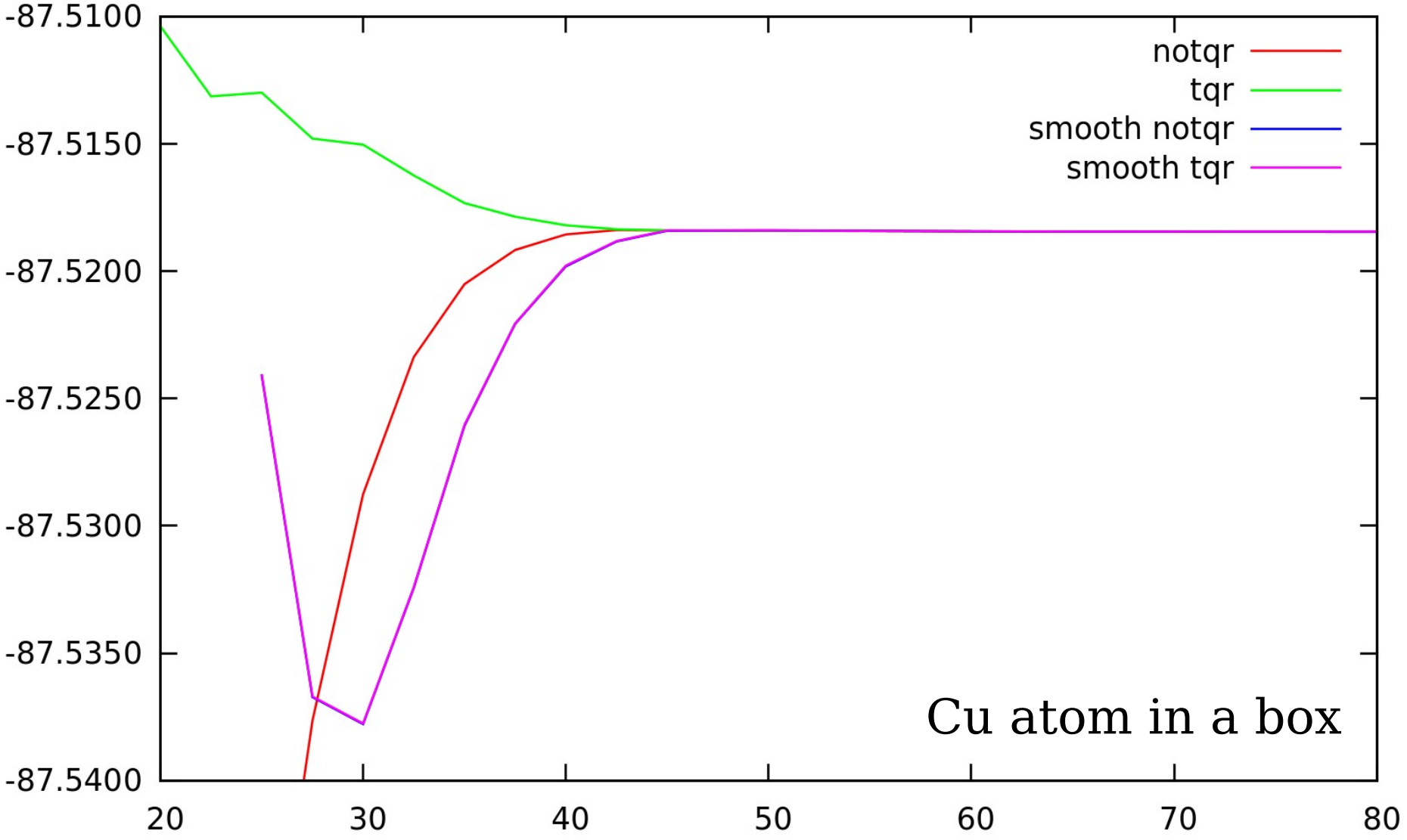
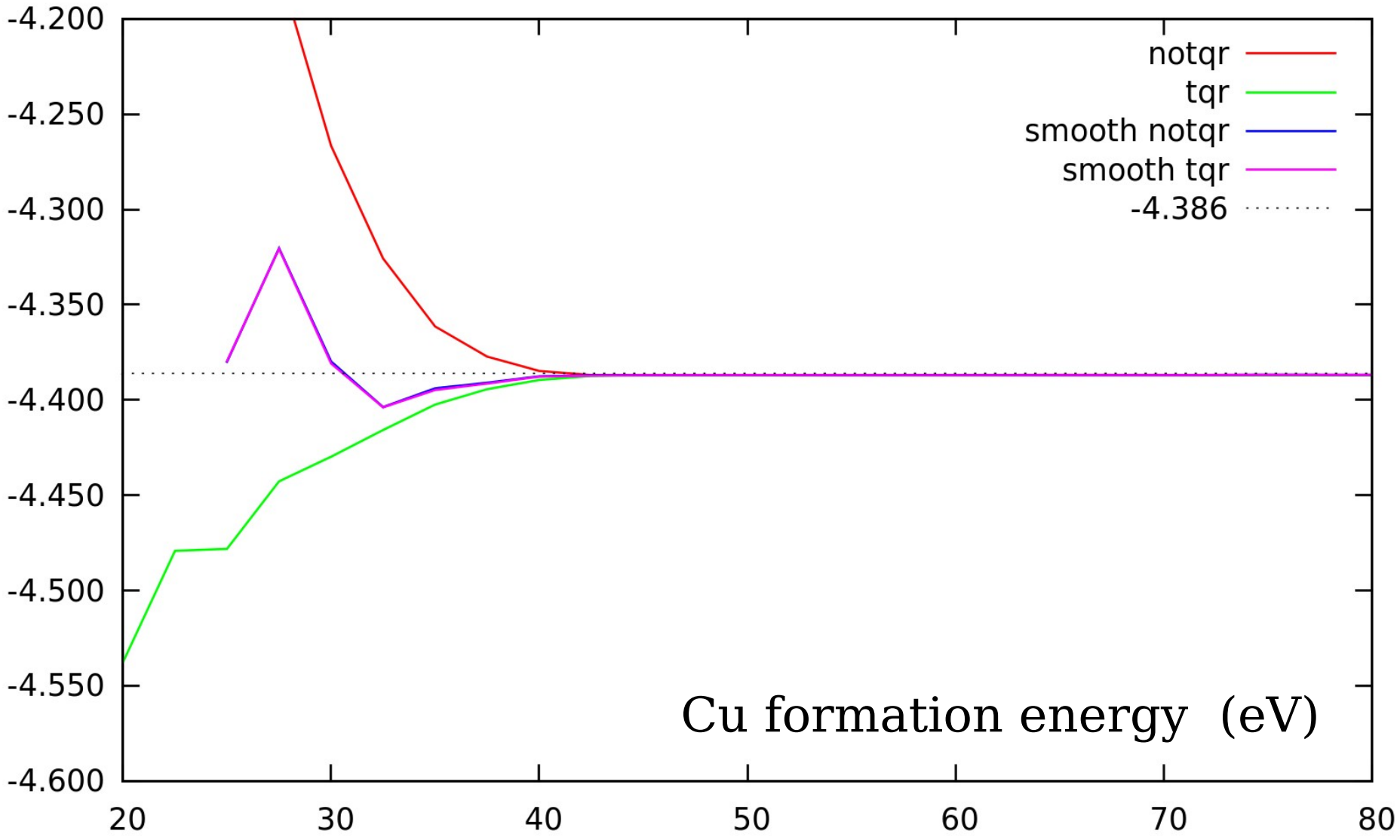


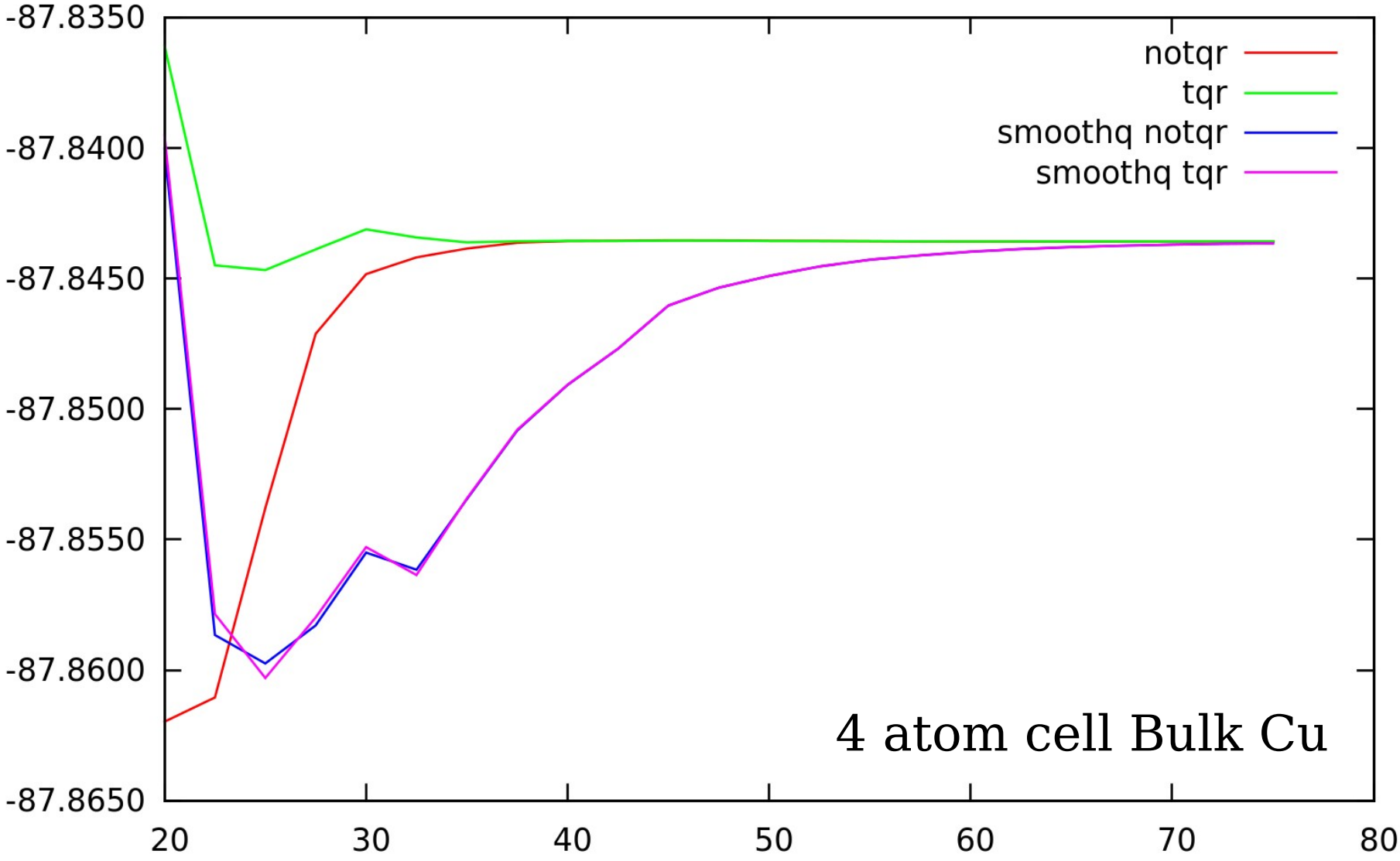
Energy vs Ecutwfc,Ecutrho=4*Ecutwfc



Energy vs Ecutwfc,Ecutrho=4*Ecutwfc



Energy vs Ecutwfc,Ecutrho=4*Ecutwfc



Energy vs Ecutwfc,Ecutrho=4*Ecutwfc

SUMMARY