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SPRING COLLEGE ON NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY

(7 - 25 May 2001)

"Brillouin-zone integration: special points and smearing techniques"

presented by:

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- A. Baldereschi Phys. Rev. B 7, 5212 (1973)
  "Mean-Value Point in the Brillouin Zone"

- D.J. Chadi and M. Cohen
  Phys. Rev. B 8, 5747 (1973)
  "Special Points in the Brillouin Zone"

- H.J. Monkhorst and J.D. Pack
  Phys. Rev. B 13, 5188 (1976)
  "Special Points for Brillouin-zone integrations"

- D.J. Chadi and M. Cohen
  Phys. Rev. B 16, 1746 (1977)
  "Special Points for Brillouin zone integrations"

- J.D. Pack and H.J. Monkhorst
  Phys. Rev. B 16, 1748 (1977)
  "Special Points for BZ integrations" - a reply

see also
S.L. Cunningham, Phys. Rev B 10, 4988 (1974)
for special points in the hexagonal lattice.

(SC)	$\{\vec{R}\}$	R^2	#	$\sum_R e^{+iRk} = G_\Sigma(k)$
Σ_0	$(0,0,0)$	0	1	1
Σ_1	$(0,0,\pm1)$	1	6	$[\cos(2\pi k_x) + \cos(2\pi k_y) + \cos(2\pi k_z)] \times 2$
Σ_2	$(0,\pm1,\pm1)$	2	12	$[\cos(2\pi k_x)\cdot\cos(2\pi k_y) + \cos(2\pi k_x)\cdot\cos(2\pi k_z) + \cos(2\pi k_y)\cdot\cos(2\pi k_z)] \cdot 4$
Σ_3	$(\pm1,\pm1,\pm1)$	3	8	$[\cos(2\pi k_x)\cos(2\pi k_y)\cdot\cos(2\pi k_z)]\,8$
	⋮			

$$\frac{\Omega}{(2\pi)^3}\int d^3k\, f(k) = \frac{\Omega}{(2\pi)^3}\int d^3k \left[\sum_R A(R)\, e^{+iRk}\right]$$

$$= \frac{\Omega}{(2\pi)^3}\int d^3k \left[\sum_\Sigma A(\Sigma)\left(\sum_{R\in\Sigma} e^{+iRk}\right)\right]$$

$$= \sum_\Sigma A(\Sigma)\left(\frac{\Omega}{(2\pi)^3}\int d^3k \sum_{R\in\Sigma} e^{+iRk}\right) = A(\Sigma_3)$$

Now $G_{\Sigma_0}(k) = 1 \quad \forall k$

for $\vec{k}^* = \left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$: $G_{\Sigma_1}(k^*) = 0$, $G_{\Sigma_2}(k^*) = 0$, $G_{\Sigma_3}(k^*) = 0$

but in general $G_{\Sigma_i}(k^*) \neq 0$ for $i > 3$

fcc $\{\vec{R}\}$ R^2 # $\sum_R e^{+iRk} = G_\Sigma(k)$

Σ_0 $(0,0,0)$ 0 1 1

Σ_1 $(\pm\frac{1}{2},\pm\frac{1}{2},0)$ $\frac{1}{2}$ 12 $[\cos(k_x\pi)\cos(k_y\pi) + \cos(k_x\pi)\cos(k_z\pi) + \cos(k_y\pi)\cos(k_z\pi)] \cdot 4$

Σ_2 $(\pm 1,0,0)$ 1 6 $[\cos(2\pi k_x) + \cos(2\pi k_y) + \cos(2\pi k_z)] \cdot 2$

Σ_3 $(\pm 1,\pm\frac{1}{2},\pm\frac{1}{2})$ 3/2 24 $[\cos(2\pi k_x)\cdot\cos(\pi k_y)\cos(\pi k_z) + \cos(\pi k_x)\cdot\cos(2\pi k_y)\cdot\cos(\pi k_z) + \cos(\pi k_x)\cdot\cos(\pi k_y)\cdot\cos(2\pi k_z)] \cdot 8$

⋮

Now $G_{\Sigma_0}(k) = 1 \quad \forall k$

the system of equations $G_{\Sigma_1}(k^*) = 0$, $G_{\Sigma_2}(k^*) = 0$
has ∞ solutions but
the system $G_{\Sigma_1}(k^*) = 0$, $G_{\Sigma_2}(k^*) = 0$, $G_{\Sigma_3}(k^*) = 0$
has NO solutions ...

$\Rightarrow k^* = (0.6223, 0.2953, 0)$
solves $G_{\Sigma_1}(k^*) = 0$, $G_{\Sigma_2}(k^*) = 0$ and minimizes $|G_{\Sigma_3}(k^*)|$

bcc $\quad \{\vec{R}\} \quad R^2 \quad \# \quad \sum_R e^{+i\vec{G}\vec{r}} = G_\Sigma(k)$

$\Sigma_0 \quad (000) \quad 0 \quad 1 \quad 1$

$\Sigma_1 \quad (\pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}) \quad \frac{3}{4} \quad 8 \quad \cos(\pi k_x)\cos(\pi k_y)\cos(\pi k_z)\cdot 8$

$\Sigma_2 \quad (\pm 1, 0, 0) \quad 1 \quad 6 \quad [\cos(2\pi k_x) + \cos(2\pi k_y) + \cos(2\pi k_z)]\cdot 2$

$\Sigma_3 \quad (\pm 1, \pm 1, 0) \quad 2 \quad 12 \quad [\cos(2\pi k_x)\cos(2\pi k_y) + \cos(2\pi k_x)\cdot\cos(2\pi k_z) + \cos(2\pi k_y)\cdot\cos(2\pi k_z)]\cdot 4$

$\vdots$

$G_{\Sigma_0}(k^*) = 1 \quad \forall k^*$

the system $G_{\Sigma_1}(k^*) = G_{\Sigma_2}(k^*) = 0$ has ∞ solutions

the system $G_{\Sigma_1}(k^*) = G_{\Sigma_2}(k^*) = G_{\Sigma_3}(k^*) = 0$ has NO solutions

$\Rightarrow k^* = (\frac{1}{6}, \frac{1}{6}, \frac{1}{2})$

solves $G_{\Sigma_1}(k^*) = G_{\Sigma_2}(k^*) = 0$ and minimizes $|G_{\Sigma_3}(k^*)|$

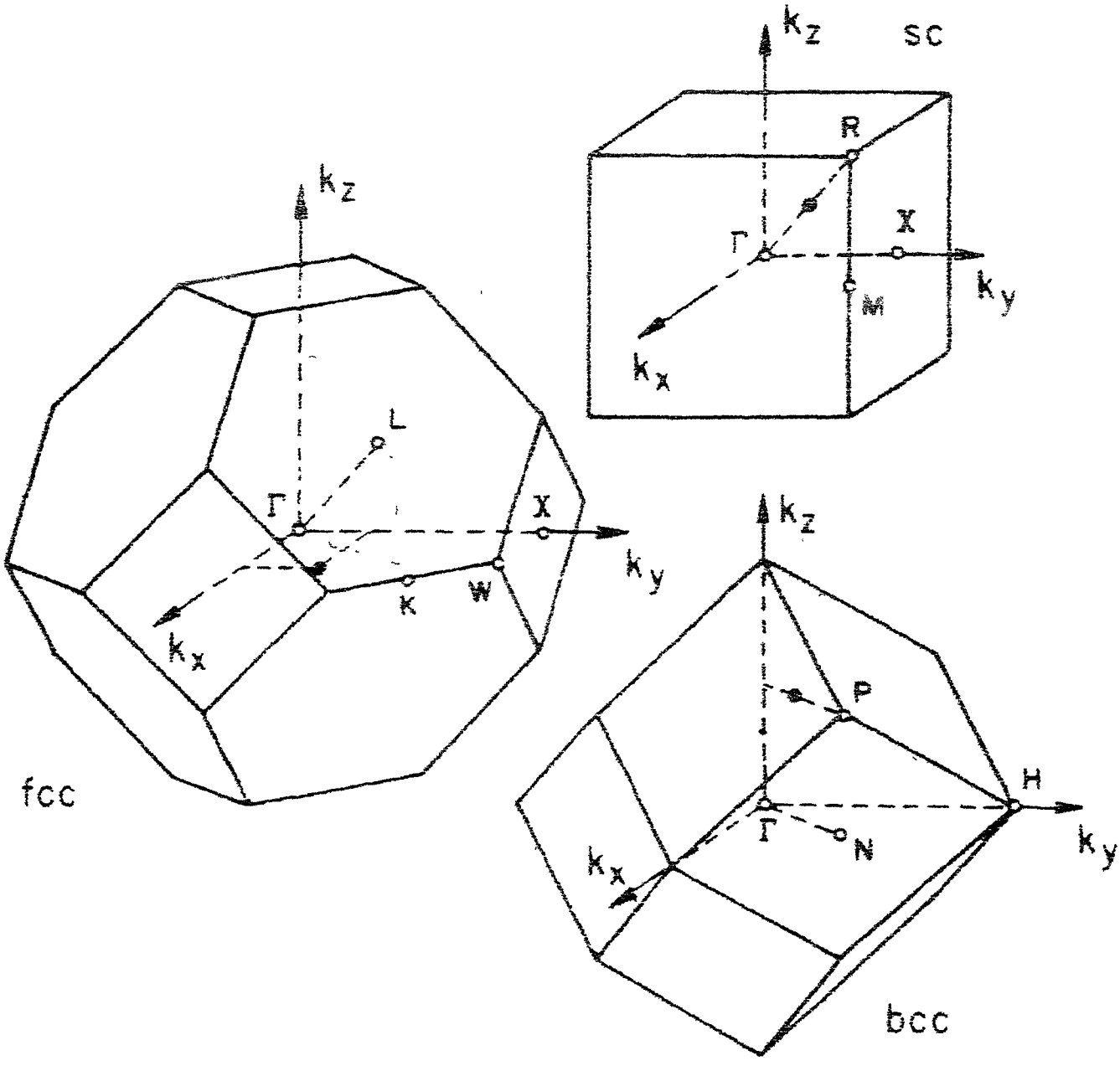


FIG. 1. Mean-value point in the Brillouin zone of different cubic lattices. Solid circles are the mean-value points, whereas open circles indicate high-symmetry points.

how one can improve w.r.t. mean-value of ?

fcc

	$G^{(k)}_{\Sigma_0}$	$G^{(k)}_{\Sigma_1}$	$G^{(k)}_{\Sigma_2}$	$G^{(k)}_{\Sigma_3}$
$K^* = (0.6223, 0.2953, 0)$	1	0	0	$\neq 0$
$K_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	1	6	0	0
$K_2 = (\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$	1	-2	0	0
$\frac{1}{4}f(K_1) + \frac{3}{4}f(K_2)$	1	0	0	0

actually this is zero up to Σ_7

$K_1 = (\frac{7}{8}, \frac{3}{8}, \frac{1}{8})$, $w_1 = \frac{6}{32}$

$K_2 = (\frac{7}{8}, \frac{1}{8}, \frac{1}{8})$, $w_2 = \frac{3}{32}$

$K_3 = (\frac{5}{8}, \frac{5}{8}, \frac{1}{8})$, $w_3 = \frac{3}{32}$

$K_4 = (\frac{5}{8}, \frac{3}{8}, \frac{3}{8})$, $w_4 = \frac{3}{32}$

$K_5 = (\frac{5}{8}, \frac{3}{8}, \frac{1}{8})$, $w_5 = \frac{6}{32}$

$K_6 = (\frac{5}{8}, \frac{1}{8}, \frac{1}{8})$, $w_6 = \frac{3}{32}$

$K_7 = (\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$, $w_7 = \frac{1}{32}$

$K_8 = (\frac{3}{8}, \frac{3}{8}, \frac{1}{8})$, $w_8 = \frac{3}{32}$

$K_9 = (\frac{3}{8}, \frac{1}{8}, \frac{1}{8})$, $w_9 = \frac{3}{32}$

$K_{10} = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$, $w_{10} = \frac{1}{32}$

$$\sum_{\alpha=1}^{10} w_\alpha = 1$$

$$\sum_{\alpha=1}^{10} w_\alpha G^{(K_\alpha)}_{\Sigma_n} = 0$$

$\forall n: \; 0 < n \leq 36$

$n = 37$ gives $\Sigma \neq 0$

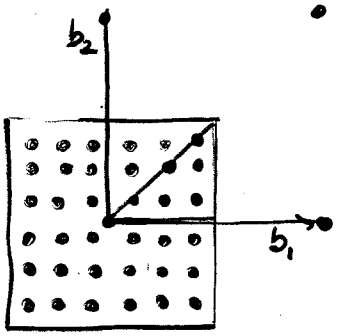
the weights are proportional to the number of K vectors belonging to the same star

BZ integrals

$$\frac{1}{N_k}\sum_k f(k) = \langle f \rangle_{BZ}$$

$$f(k) = \sum_R f_R e^{+ikR} \Rightarrow \langle f \rangle_{BZ} = f_0$$

a regular grid with $\Delta k = \frac{2\pi}{a}\frac{1}{N}$ integrate exactly up to $R_{MAX} = \frac{Na}{2}$ (in a cubic system)



If some symmetry is present it can be exploited in order to compute only the k-point in the irreducible wedge of the BZ

$$S(R+\tau_s) + f = R' + \tau_s'$$

Monkhorst and Pack
Phys. Rev. B 13 5188 (76)

$$\psi_{Sk,\nu}(r) = \psi_{k,\nu}(S^{-1}r - f)$$

$\{\vec{k}_i, w_i\}$ with $\sum_i w_i = 1$ and $\vec{k}_i \in IBZ$

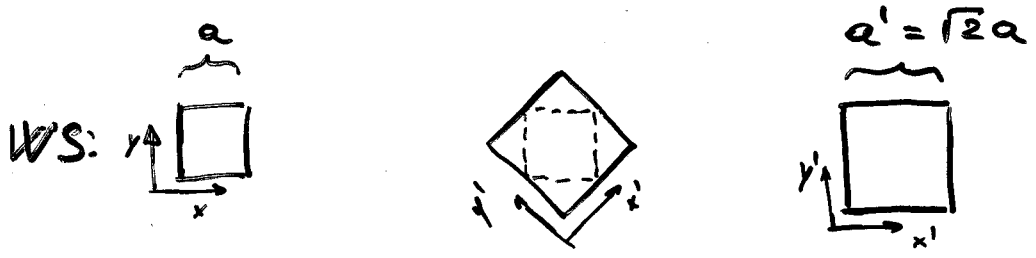
$\tilde{\rho}(r) = \sum_i w_i |\psi_{k_i}(r)|^2$ unsymmetrized density

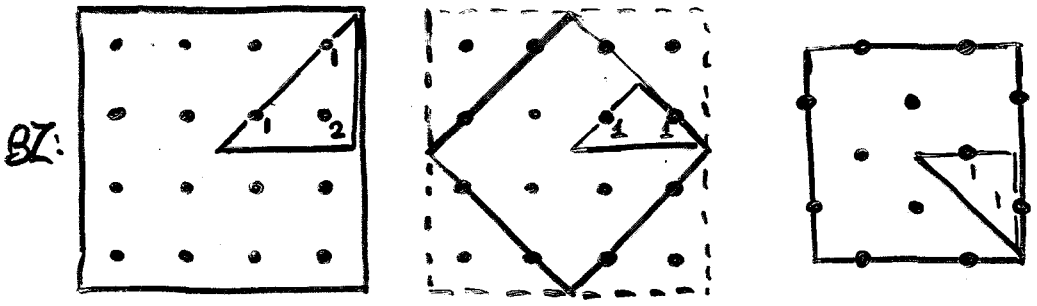
$$\rho(r) = \frac{1}{N_{sym}} \sum_S \tilde{\rho}(S^{-1}r - f)$$

The needed R_{MAX} is of the order of the spatial extent of the Wannier functions of the solid a few bond lengths

For large systems the BZ is small and the bands flat $\Rightarrow \langle f \rangle_{BZ} \simeq f(\Gamma)$

When performing calculations in Supercells (Defects, Alloys, Superlattices, Frozen Phonons) it is often convenient to use k-points that are "equivalent" to those used in the bulk calculation in order to make the different energies exactly comparable.





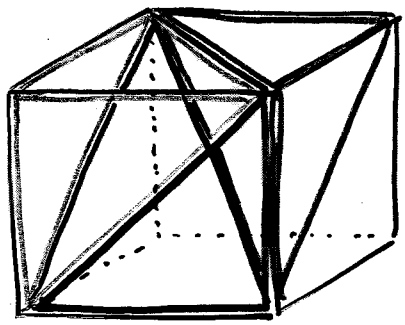
If the symmetry of the crystal structure is lower than the symmetry of the Bravais lattice the number of inequivalent points increases and their weight changes

Special Points for superlattices
S.Y. Ren - J.D. Dow Phys. Rev. 38, 1999 (1988)

Tetrahedra

given a regular grid of $\vec{k}$ in the BZ

any small cube can be split in 6 tetrahedra that completely fill it



within each tetrahedron each energy band can be linearly interpolated

from each of the interpolated bands one can analytically calculate the fraction of the tetrahedron that corresponds to occupied states and then the weight of it

explicit formulas can be found in

Skriver, "the LMTO method" Springer-Verlag

Smearing techniques

$$n(r) = 2 \sum_{\nu} \frac{\Omega}{(2\pi)^3} \int d^3k \; \vartheta(\varepsilon_F - \varepsilon_\nu(k)) \; |\varphi^{(r)}_{k\nu}|^2$$

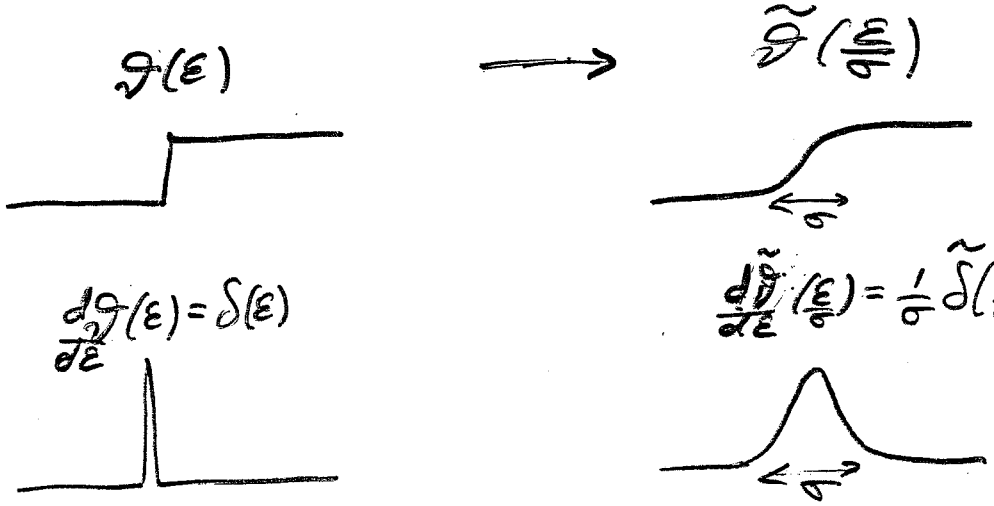
(spin degeneracy)

we actually use a discret grid

$$n(r) = 2 \sum_{\nu} \frac{1}{N_k} \sum_{k_i} \vartheta(\varepsilon_F - \varepsilon_\nu(k_i)) \; |\varphi^{(r)}_{k_i\nu}|^2$$

the step function makes this integral badly convergent.

Possible solution: smooth the integral by substituting $\vartheta(\varepsilon)$ with a smoother function



the larger is σ the smoother is the function and therefore smaller the number of k-points in the grid needed to integrate accurately

Unfortunately

the larger is σ the more the function differs from the original one and the integral deviates from the $\sigma \to 0$ limit that corresponds to the physical situation.

Several smearing functions have been proposed

Fermi-Dirac

$$\vartheta(x) = \frac{1}{1+\exp(-x)} \qquad \delta(x) = \frac{1}{2+\exp(x)+\exp(+x)}$$

Gaussian: Fu and Ho, PRB 28, 5480 (1983)

$$\vartheta(x) = A \cdot \mathrm{erf}(x) \qquad \delta(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}}$$

Gaussian times polynomials
Methfessel and Paxton PRB 40 3616 (1989)
Marzari and Vanderbilt PRL (1998)?

$$\vartheta(x) = \int_{-\infty}^{x} \delta(y)\,dy \qquad \delta(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} P(x)$$

It can be shown that the "correct" energy is

$$E = 2\sum_{kv} \vartheta\left(\frac{\varepsilon_F - \varepsilon_{kv}}{\sigma}\right) \langle \psi_{kv} | -\frac{\hbar^2}{2m}\nabla^2 | \psi_{kv} \rangle + \int V_0(r)\, n(r)\, d^3r$$

$$+ \frac{e^2}{2}\int \frac{n(r)\, n(r')}{|r-r'|} d^3r\, d^3r' + E_{xc}[n] + \sigma \sum_{kv} \vartheta_1\left(\frac{\varepsilon_F - \varepsilon_{kv}}{\sigma}\right)$$

for Fermi-Dirac smearing

$$\vartheta_1(x) = \int_{-\infty}^{x} y \frac{d}{dy}\left(\frac{1}{1+e^{-y}}\right) dy = \frac{x}{1+\exp(-x)} - \ln(1+\exp(x))$$

$$= \vartheta \ln \vartheta + (1-\vartheta)\ln(1-\vartheta)$$

that is the expression for the entropy for non interacting electrons.
In fact in this case E is actually the Free Energy

since $\frac{dF}{dT} = -S$ we have (also for general smearing)

$$\frac{dE}{d\sigma} = \sum_{kv} \vartheta_1\left(\frac{\varepsilon_F - \varepsilon_{kv}}{\sigma}\right) \cong \int_{-\infty}^{\infty} d\varepsilon\, n(\varepsilon) \int_{-\infty}^{(\varepsilon_F - \varepsilon)/\sigma} y\, d(y)\, dy$$

$$= -\sum_{k=0}^{\infty} \sigma^{2k+1} \frac{c_{k+1}}{(2k+1)!} \left.\frac{d^{2k} n}{d\varepsilon^{2k}}\right|_{\varepsilon_F}$$

$$c_k = \int_{-\infty}^{\infty} x^2 \delta(x)\, dx$$

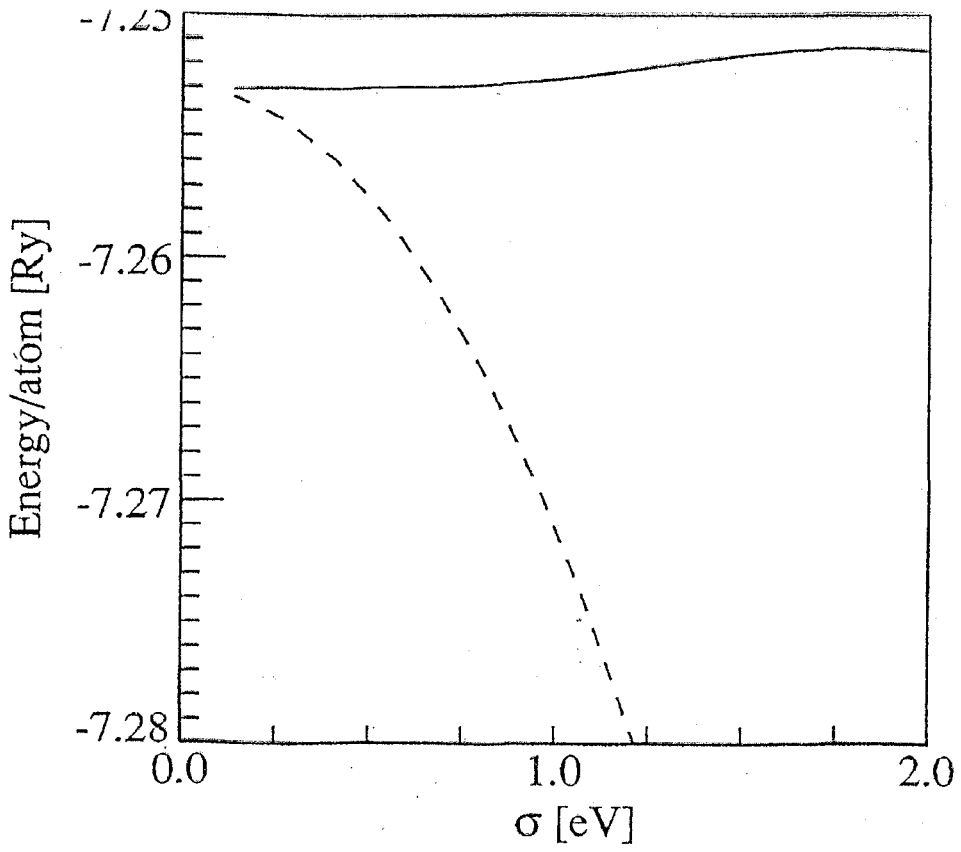


FIG. 1. Total energy per atom of fcc-Pb crystal as a function of the smearing linewidth and for two different smearing functions: the Hermite-Gaussian function of order 1 (solid line) and the simple Gaussian function (dashed line).