Thesis: $\int_{-\infty}^{\infty} \rho_i(E)\, E\, dE = \varepsilon_i$

with: $\rho_i(E)$ = partial density of states with character ϕ_i
ϕ_i = a basis function
$\varepsilon_i = \langle \phi_i | H | \phi_i \rangle$

use: application of this formula yield the on-site energies of local atomic orbitals used in a bandstructure calculation.

Proof:

Basis ϕ_i, with energy $\varepsilon_i = \langle \phi_i | H | \phi_i \rangle$
and $\exists_{ij} : \langle \phi_i | H | \phi_j \rangle \neq 0$,
$\langle \phi_i | \phi_j \rangle = \delta_{ij}$, $\sum_i |\phi_i\rangle\langle\phi_i| = 1$

Eigenfunctions ψ_ℓ, with energy $E_\ell = \langle \psi_\ell | H | \psi_\ell \rangle$
and $\langle \psi_\ell | H | \psi_m \rangle = E_\ell \cdot \delta_{\ell m}$,
$\langle \psi_\ell | \psi_m \rangle = \delta_{\ell m}$, $\sum_\ell |\psi_\ell\rangle\langle\psi_\ell| = 1$

$$\psi_\ell = \sum_i \alpha_{\ell i}\, \phi_i \quad \rightarrow \quad \alpha_{\ell i} = \langle \phi_i | \psi_\ell \rangle$$

$$\rho_i \equiv |\alpha_{\ell i}|^2$$

$$\int_{-\infty}^{\infty} \rho_i(E)\, E\, dE = \sum_\ell |\alpha_{\ell i}|^2 E_\ell = \sum_\ell \langle \phi_i | \psi_\ell \rangle \langle \psi_\ell | \phi_i \rangle E_\ell$$

$$= \sum_m \sum_\ell \langle \phi_i | \psi_\ell \rangle E_\ell \cdot \delta_{\ell m} \langle \psi_\ell | \phi_i \rangle$$
$$= \sum_m \sum_\ell \langle \phi_i | \psi_\ell \rangle E_\ell \cdot \delta_{\ell m} \langle \psi_m | \phi_i \rangle$$
$$= \sum_m \sum_\ell \langle \phi_i | \psi_\ell \rangle \langle \psi_\ell | H | \psi_m \rangle \langle \psi_m | \phi_i \rangle$$
$$= \langle \phi_i | H | \phi_i \rangle = \varepsilon_i \qquad \text{q.e.d.}$$