

Zunger and Freeman 1977a, b, c, 1978) or model potentials (Wendel and Martin 1978). Unlike the situation in molecular physics, we have in this case to deal with divergent terms. Moreover, the calculation of the total energy poses a practical difficulty associated with the need to compute a large number of six-dimensional integrals for the electron-electron interaction term. In linear band structure approaches (e.g. linear combination of atomic orbitals), this leads to a large number of multicentre integrals (Schaefer 1972, Harris and Monkhorst 1971, Wepfer *et al* 1974).

This major difficulty has led to a number of 'shape approximations' in which the charge density $\rho(\mathbf{r})$ is replaced by a radially scalar quantity such as the muffin-tin (DeGroot

is readily applicable to calculations with mixed basis sets (e.g. plane wave plus Gaussian) as well. This enables us to extend our calculations to the case of transition metals.

The virtue of the present method rests in its computational simplicity; once we perform the band structure calculation, the total energy is automatically obtained as a sum of a few previously calculated terms without multicentre interactions. The only

equation (1) is the density functional exchange–correlation contribution to the total energy (Hohenberg and Kohn 1964, Kohn and Sham 1965).

The corresponding one-electron Schrödinger equation is written as follows:

Coulomb repulsion energy becomes:

$$\frac{1}{2} \iint \frac{2\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' = \frac{1}{2}\Omega \sum_{\mathbf{G}} V_{\text{Coul}}(\mathbf{G}) \rho(\mathbf{G}). \quad (8)$$

Using the translational invariance and the decomposition of the plane waves into spherical harmonics and Bessel functions, the pseudopotential energy can be written as:

$$\begin{aligned} & \sum_{i,\mu,l} \int \psi_i^*(\mathbf{r}) U_{\text{ps},l}(\mathbf{r}-\mathbf{R}_\mu) \hat{P}_l \psi_i(\mathbf{r}) d^3r \\ &= \Omega \sum_{i,l,\mathbf{G},\mathbf{G}'} \psi^*(\mathbf{k}_i+\mathbf{G}) \psi(\mathbf{k}_i+\mathbf{G}') \sum_{\mu} \frac{\exp[i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{R}_\mu]}{N} \\ & \times (1/\Omega_{\text{at}}) \int \exp[-i(\mathbf{k}_i+\mathbf{G})\cdot\mathbf{r}] U_{\text{ps},l}(\mathbf{r}) \hat{P}_l \exp[i(\mathbf{k}_i+\mathbf{G}')\cdot\mathbf{r}] d^3r \\ &= \Omega \sum_{i,l,\mathbf{G},\mathbf{G}'} \psi^*(\mathbf{k}_i+\mathbf{G}) \psi(\mathbf{k}_i+\mathbf{G}') S(\mathbf{G}'-\mathbf{G}) U_{\text{ps},l}(\mathbf{G},\mathbf{G}') \end{aligned} \quad (9)$$

disappears for large r). We still have infinite degrees of freedom for behaviour of $U_{ps}(r)$ at small values of r . If required, $U_{ps}(r)$ can be chosen such that both $U_{ps}(r)$ and $U'_{ps,l}(r)$

where the prime means that $P = 0$ is excluded in the summation. Combining equations

extreme case of the transition metals Mo and W (Zunger and Cohen 1979) (characterised by localised d states). We have found that a convergence of 3 mRyd in the individual momentum sums can be reached by including about 500, 200 and 200 plane waves

defined by

$$\sum_i [\hat{P}_i \psi_i(\mathbf{r})]^+ \hat{P}_i \psi_i(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \hat{P}_i \psi_i(\mathbf{r}) \equiv \rho_{\text{elec},i}(\mathbf{r}). \quad (30)$$

Note that $\rho_{\text{elec},i}(\mathbf{r})$ is not identical to $\hat{P}_i \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) = \hat{P}_i \rho(\mathbf{r})$. Now we take the gradient of the first term on the right-hand side of equation (3),

$$\begin{aligned} -\nabla_{\mathbf{R}_\mu} \sum_i \int \psi_i^*(\mathbf{r}) \sum_{l,v} U_{\text{ps},l}(\mathbf{r} - \mathbf{R}_v) \hat{P}_i \psi_i(\mathbf{r}) d^3r \\ = -\sum_i \int \psi_i^*(\mathbf{r}) \sum_l [\nabla_{\mathbf{R}_\mu} U_{\text{ps},l}(\mathbf{r} - \mathbf{R}_\mu)] \hat{P}_i \psi_i(\mathbf{r}) d^3r = \sum_i \int \psi_i^*(\mathbf{r}) \sum_l \\ \times [\nabla_r U_{\text{ps},l}(\mathbf{r} - \mathbf{R}_\mu)] \hat{P}_i \psi_i(\mathbf{r}) d^3r. \end{aligned} \quad (31)$$

Using the identity

$$V(\mathbf{r}) = -\frac{1}{4\pi} \int \frac{\nabla_r^2 V(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r', \quad (32)$$

equation (31) becomes

$$\begin{aligned} \sum_i \int \psi_i^*(\mathbf{r}) \sum_l \nabla_r \left(-\frac{1}{4\pi} \int \frac{\nabla_{r'}^2 U_{\text{ps},l}(\mathbf{r}' - \mathbf{R}_\mu) d^3r'}{|\mathbf{r} - \mathbf{r}'|} \right) \hat{P}_i \psi_i(\mathbf{r}) d^3r \\ = \sum_i \int \psi_i^*(\mathbf{r}) \sum_l \int \left(-\frac{1}{4\pi} \nabla_{r'}^2 U_{\text{ps},l}(\mathbf{r}' - \mathbf{R}_\mu) \right) \left(\nabla_r \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) d^3r' \hat{P}_i \psi_i(\mathbf{r}) d^3r \\ = \sum_l \int \left[-\frac{1}{4\pi} \nabla_{r'}^2 U_{\text{ps},l}(\mathbf{r}' - \mathbf{R}_\mu) \right] \left(-\nabla_{r'} \int (\sum_i \psi_i^*(\mathbf{r}) \hat{P}_i \psi_i(\mathbf{r}) / |\mathbf{r} - \mathbf{r}'|) d^3r \right) \\ d^3r' = \nabla_{r'} \int \rho_{\text{elec},i}(\mathbf{r}) / |\mathbf{r}' - \mathbf{R}_\mu| d^3r = \mathbf{E} \end{aligned} \quad (33)$$

$$\mathbf{E}_i(\mathbf{r}') = -\nabla_{r'} \int \frac{\rho_{\text{elec},i}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3r \quad (34)$$

is the effective electric field produced by electrons and experienced by ψ_i . It reduces

In the local pseudopotential approximation, equation (35) is reduced as

$$F_{2, \text{local}} = -\nabla_{R_\mu} \Omega \sum_{\nu, \mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{R}_\nu) N^{-1} U_{\text{ps}}(\mathbf{G}) \rho(\mathbf{G}) = -i\Omega_{\text{at}} \sum_{\mathbf{G}} \mathbf{G} \exp(i\mathbf{G} \cdot \mathbf{R}_\mu) \times U_{\text{ps}}(\mathbf{G}) \rho(\mathbf{G}). \quad (36)$$

Summarising, the Hellmann–Feynman theorem in the momentum-space is

$$-\nabla_{R_\mu} E_{\text{total}} = -\nabla_{R_\mu} \sum_{\substack{\nu \\ \nu \neq \mu}} \frac{2Z^2}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} - i\Omega_{\text{at}} \sum_{i, l, \mathbf{G}, \mathbf{G}'} (\mathbf{G}' - \mathbf{G}) \exp[i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{R}_\mu] \times \psi^*(\mathbf{k}_i + \mathbf{G}) \psi(\mathbf{k}_i + \mathbf{G}') U_{\text{ps}, l, \mathbf{k}_i + \mathbf{G}, \mathbf{k}_i + \mathbf{G}'}. \quad (37)$$

Possible applications of the theorem are diverse. For example, we can study the equilibrium configuration of the surface atoms, the surface chemisorption, effects of the impurities and defects in the bulk and the surface, or the phonon modes of solids.

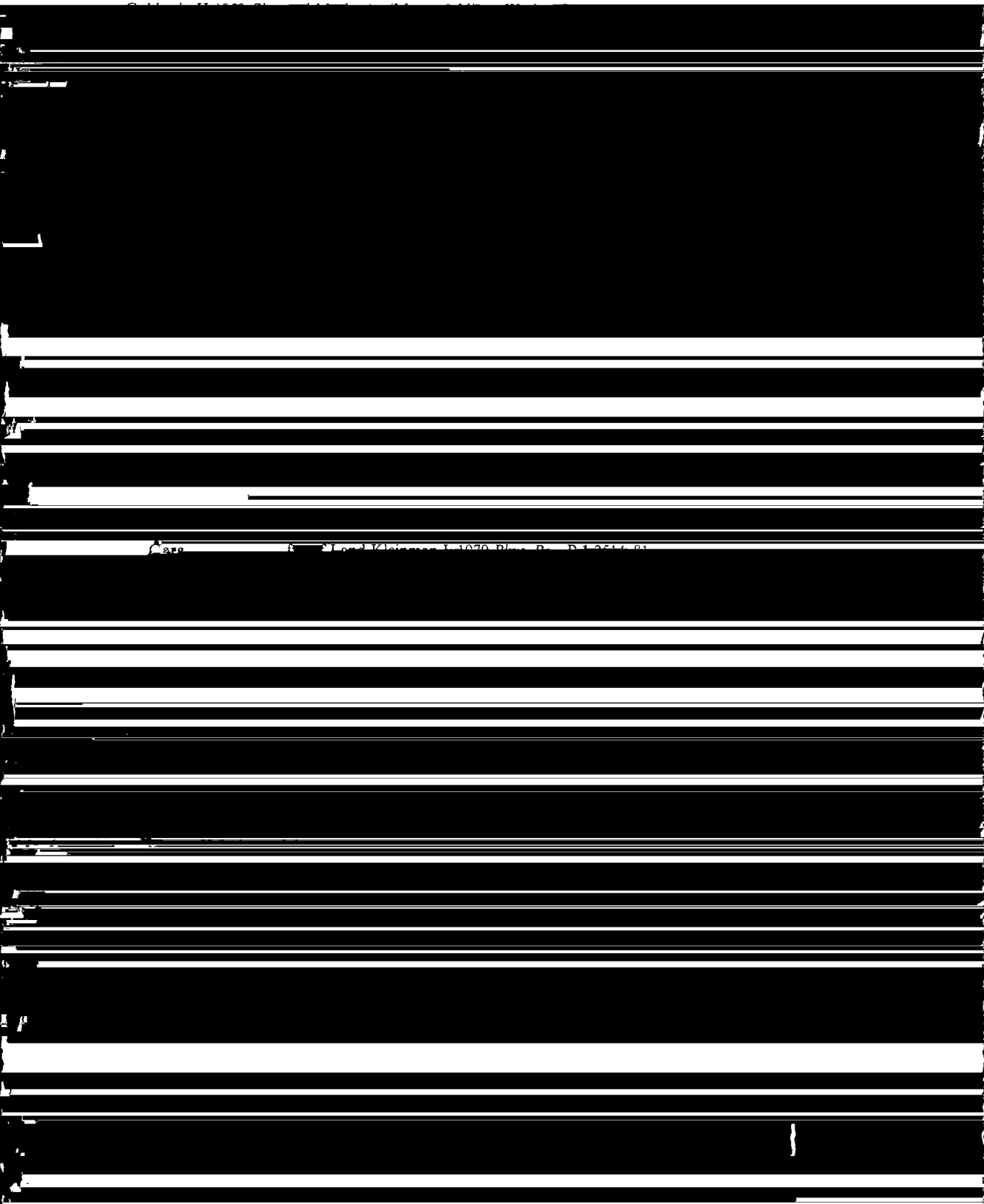
4. Virial theorem

It is a well known fact of classical mechanics that the time average of the bounded motion

conclusion that equation (39) is to be modified for the pseudopotential Hamiltonian as follows:

$$\begin{aligned} \text{KE} = & -\frac{1}{2}\text{PE} - \frac{1}{2} \sum_{\mu} \mathbf{R}_{\mu} \cdot \nabla_{\mathbf{R}_{\mu}} E_{\text{total}} \\ & + \frac{1}{2} \sum_{i,l,\mu} \int \psi_i^*(\mathbf{r}) \left(U_{\text{ps},l}(\mathbf{r}') + \mathbf{r}' \cdot \frac{\partial U_{\text{ps},l}(\mathbf{r}')}{\partial \mathbf{r}'} \right)_{\mathbf{r}'=\mathbf{r}-\mathbf{R}_{\mu}} \hat{P}_l \psi_i(\mathbf{r}) d^3r. \end{aligned} \quad (42)$$

The difference between the all-electron case (equation 39) and the pseudopotential case (equation 42) originates primarily from the cancellation theorem. The correction term in equation (42) which is usually a large negative quantity represents the reduction of



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