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Short Communication

Comparison of two expressions to compute the electronic energy of a crystal

Š. Pick

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-182 23 Prague 8, Czechoslovakia

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Abstract. — Two expressions for the electronic energy, the second one of which is not selfconsistent, are analyzed. It appears that the two formulas are equivalent up to the first order in selfconsistent corrections.

Several years ago, the legitimacy of two formulas for the electronic (band) energy change has been discussed by Masuda-Jindo et al. [1]. The two formulas read

\[ \Delta E = \sum_A \left[ \int_{E_F}^{E} E \Delta \rho_A(E) \, dE - \Delta \phi_A N_A \right] \]  

(1)

and

\[ \Delta E = \sum_A \int_{E_F}^{E} (E - E_F) \Delta \rho_A(E) \, dE, \]  

(2)

respectively. Above, \( \Delta \rho_A \) is the change of the local partial density of electronic states associated with the spin-orbital \( \alpha \) residing on the site \( i(A = (\alpha, i)) \), \( N_A = \int_{E_F}^{E_F} \rho_A \, dE \) is the occupation number and \( \phi_A \) is the Coulomb integral (diagonal matrix element of the Hamiltonian). Expressions analogous to equation (1) are commonly used in the solid state computations [1-3]. The form we adopt here is somewhat more general than that considered in [1] and it is identical to equation (11) of reference [3] apart from the second order contributions which are of the form \( \Delta \phi_A \Delta N_A / 2 \). In the important case of d-band metals, the latter terms vanish rigorously when the local charge neutrality is postulated [1, 2]. However, the local charge neutrality is not obvious [3] for validity of equation (1). To derive equation (2), two similar homogeneous crystals with slightly different Fermi level positions are considered [4]. The inclusion of the \( E_F \)-term reduces the inaccuracy inherent to equation (2) to a small term of order \( \Delta E_F \Delta N \).

In the present note, we consider two similar nonhomogeneous systems for which Fermi levels coincide (e.g. various crystal surface arrangements or bulk defects). We suppose that the expression (2) corresponds to a non-selfconsistent treatment (i.e. the global charge neutrality condition...
\[ \sum_A \Delta N_A = 0 \] can be violated. As for the equation (1), we assume that the charge selfconsistency is imposed which is controlled by the changes \( \Delta \phi_A \). The main goal of our discussion is to prove that under these assumptions, the expressions (1) and (2) are equivalent up to the first order in the perturbation introduced by the selfconsistency.

It is convenient to distinguish the geometrical (\( \Delta \)) and selfconsistent (\( \delta \)) corrections in equation (1). Namely, we introduce new notation \( \Delta \rho = \Delta \rho + \delta \rho \) and similarly for the other quantities. For the "atomic levels" \( \phi_A \) only \( \delta \phi_A \) does not vanish. We treat the \( \delta \)-component of equation (1) as a perturbation. By introducing the Green function \( G(z) \) \( (z = E + i\delta) \), we transform the equation (1) to the form

\[ \delta E = -\pi^{-1} \sum_A \text{Im} \int_{E_F}^{E} [\delta G_{AA}(z) E - \delta \phi_A G_{AA}(z)] \, dE. \]  

(3)

To the first order,

\[ \sum_A \delta G_{AA} = \sum_{AB} G_{AB} \delta \phi_B G_{BA} = -\sum_B \delta \phi_B dG_{BB}/dE. \]  

(4)

(Here and below, we use the identity \( G^2 = -dG/dz \).) Inserting equation (4) into equation (3) and integrating by parts we find

\[ \delta E = \pi^{-1} \sum_A \text{Im} \delta \phi_A E_F G_{AA} \, (E_F + i\delta). \]  

(5)

Further manipulations yield

\[ \delta E = \pi^{-1} \sum_A \text{Im} \delta \phi_A E_F \int_{E_F}^{E} dG_{AA}/dE \, dE \]

\[ = -\pi^{-1} \sum_{AB} \text{Im} E_F \int_{E_F}^{E} G_{AB} G_{BA} \delta \phi_A dE = -\pi^{-1} \sum_A \text{Im} E_F \int_{E_F}^{E} \delta G_{AA} \]

\[ = E_F \sum_A \delta N_A. \]  

(6)

The selfconsistency grants, however, the global charge neutrality:

\[ \sum_A (\delta N_A + \Delta N_A) = 0. \]  

(7)

By virtue of the latter identity,

\[ \delta E = -\sum_A E_F \Delta N_A = -\sum_A \int_{E_F}^{E} E_F \Delta \rho_A. \]  

(8)

which proves the equivalence of the expressions (1), (2) in the sense claimed above.

The result arrived at gives some justification to the attempts to investigate in a highly simplified manner low symmetry systems for which a rigorous treatment becomes cumbersome. Another point worth of attention is the fact that whatever the selfconsistency procedure be (local charge neutrality, inclusion of Hubbard-like terms, special electronegativity adjustment), the resulting energy change is the same up to the first order in the selfconsistency corrections. Indeed, the only explicit selfconsistency condition we have employed is the global charge neutrality (7).
References


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