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# Ground-state energy of many-electron systems from x-ray-scattering cross sections

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In the nonrelativistic limit and for a purely electrostatic Hamiltonian, an exact relation between the ground-state energy of a crystal and the x-ray-scattering cross section has been derived which allows us to distinguish static from dynamical (exchange and correlation) contributions. With the use of this relation and the corresponding one valid in the case of an isolated atom, it is possible to calculate the cohesive energy of a crystalline substance. Available x-ray cross-section data have been used to calculate the cohesive energy of Be, Si, Al, and Cu. In the case of Be, agreement of calculated cohesive energy with the thermochemical value is obtained if exchange and correlation contributions are included. For the other solids, a substantial disagreement increasing with atomic number has been evidenced. Poor agreement of calculated cohesive energies with thermochemical values is presumably to be attributed to a lack of sufficiently comprehensive sets of measured cross sections.

## INTRODUCTION

The well-known Hohenberg and Kohn theorem[1] states that in the nonrelativistic limit any ground-state property of a nondegenerate many-electron system is a universal functional of the electron number density.

Although the universal functionals referred to above are in general unknown, resulting in the impossibility of actually using the Hohenberg and Kohn theorem, it is possible to write an explicit relation between the x-ray cross section and the total ground-state energy of a crystal, which is the equivalent of the sum rules which in a free atom relate the x-ray cross section to the average inverse electron-nucleus and electron-electron distances.[2]

In contrast to already published approximate relations,[3] the present treatment is exact if nuclei are considered having infinite mass and if the magnetic contribution to total energy (smaller than purely electrostatic terms by several orders of magnitude[4]) is neglected. This feature allows us to put into a sharper focus the differences, when they exist, between available cross sections and known cohesive energies and to assess with better confidence the accuracy and completeness of measured and calculated cross sections.

## ENERGY EQUATIONS

Consider a system composed by a very large number of nuclei and electrons and such that it is accurately described by a nonrelativistic Hamiltonian. In this case its ground-state potential energy is given by:

$$V_0=V_{ee}+V_{e\mathcal{N}}+V_{\mathcal{N}\mathcal{N}}=\frac{e^2}{2}\int d\vec{r}\,d\vec{r}\,'\frac{1}{|\vec{r}-\vec{r}\,'|}\langle 0|\{\rho^\dagger(\vec{r})\rho(\vec{r}\,')-[\rho^\dagger(\vec{r})\rho_{\mathcal{N}}(\vec{r}\,')+\text{H.c.}]$$
$$+\rho^\dagger_{\mathcal{N}}(\vec{r})\rho_{\mathcal{N}}(\vec{r}\,')\}|0\rangle-\Sigma_{ee}-\Sigma_{\mathcal{N}\mathcal{N}}\,, \tag{1}$$

where $V_{ee}$, $V_{e\mathcal{N}}$, and $V_{\mathcal{N}\mathcal{N}}$ are the electron-electron, electron-nucleus, and nucleus-nucleus interactions, respectively, $\rho(\vec{r})$ and $\rho_{\mathcal{N}}(\vec{r})$ are the electronic and nuclear number density operators, $|0\rangle$ is the exact total-system ground state, and $\Sigma_{ee}$ and $\Sigma_{\mathcal{N}\mathcal{N}}$ are the electronic and nuclear self-energy terms. Specializing Eq. (1) to the case of an elemental system, we can write:

$$V_0=\frac{e^2}{2}\int d\vec{r}\,d\vec{r}\,'\frac{1}{|\vec{r}-\vec{r}\,'|}\left[[\langle 0|\rho^\dagger(\vec{r})\rho(\vec{r}\,')|0\rangle-n(\vec{r})n(\vec{r}\,')-\Sigma_{ee}]+n(\vec{r})n(\vec{r}\,')-2Z\sum_l n(\vec{r})\delta(\vec{r}\,'-\vec{R}_l)\right.$$
$$\left.+Z^z\sum_{l,l'}\delta(\vec{r}-\vec{R}_l)\delta(\vec{r}\,'-\vec{R}_{l'})-\Sigma_{\mathcal{N}\mathcal{N}}\right]\,, \tag{2}$$

where $Z$ is the atomic number, $n(\vec{r})$ is the electronic ground-state number density, and the $\vec{R}_l$'s are the positions of the $N$ nuclei of the system. In Eq. (2) we have divided the electron-electron contribution into a dynamical (exchange-correlation) part and into a static part.[5] In order to further simplify Eq. (2), henceforth we shall only consider crystalline systems. In this case, since $n(\vec{r})$ has the lattice periodicity it can be Fourier analyzed:

$$n(\vec{r})=\frac{1}{\Omega_0}\sum_{\vec{G}}F_{\vec{G}}\,e^{i\vec{G}\cdot\vec{r}}\,, \tag{3}$$

where the $\vec{G}$'s are reciprocal-lattice vectors, the $F_{\vec{G}}$'s are the unit-cell structure factors (calculated without the dispersion contribution to the atomic scattering factor), and $\Omega_0$ is the unit-cell volume. In a similar way also the dynamical part of the electron-electron term can be Fourier analyzed using the incoherent scattering cross section which, for an atom having $|0\rangle$ as its ground state, can be written as[6]

$$S(\vec{Q})=\sum_{m,n}\langle 0|e^{i\vec{Q}\cdot(\vec{r}_m-\vec{r}_n)}|0\rangle-|f(\vec{Q})|^2 , \tag{4a}$$

where both sums run over all electrons in the atom, $\vec{r}_m$ is the radius vector from the nucleus to the $m$th electron, and $f(\vec{Q})$ is the atomic scattering factor. In our case, using the number-density formalism, Eq. (4) is written as

$$NS(\vec{Q})=\int d\vec{r}\,d\vec{r}\,'\{e^{i\vec{Q}\cdot(\vec{r}-\vec{r}\,')}[\langle 0|\rho^{\dagger}(\vec{r})\rho(\vec{r}\,')|0\rangle-n(\vec{r})n(\vec{r}\,')]\} , \tag{4b}$$

where $S(\vec{Q})$ is now the incoherent scattering cross section per atom of the solid. Then, upon substitution of Eqs. (3) and (4b) into Eq. (2) and treating the nucleus-nucleus term by means of the well-known Ewald method,[7] one has

$$V_0=\frac{Ne^2}{2}\left[\frac{1}{2\pi^2}\int[S(\vec{Q})-Z]\frac{1}{Q^2}d\vec{Q}+\frac{4\pi}{\Omega_0}\sum_{\vec{G}}{}'\frac{|F_{\vec{G}}|^2}{G^2}-\frac{4\pi}{\Omega_0}\sum_{\vec{G}}{}'\frac{(F^*_{\vec{G}}F^g_{\vec{G}}+\text{c.c.})}{G^2}-\frac{\alpha Z^2}{r_0}\right] , \tag{5}$$

where $\sum'$ means that the (000) reciprocal-lattice vector has to be omitted, $\alpha$ is the Madelung constant of the lattice, $r_0$ is the cell radius, and $F^g_{\vec{G}}$ is the geometrical structure factor of the cell

$$F^g_{\vec{G}}=\sum_s e^{i\vec{G}\cdot\vec{r}_s} \tag{6}$$

with the index $s$ running over the nuclear positions $\vec{r}_s$ in the unit cell. Within the limits mentioned so far, Eq. (5) is exact and applicable to an elemental system of whatever crystal symmetry. Using the virial theorem whose simple form at zero external pressure is[8]

$$E_0=T_0+V_0=\frac{V_0}{2} , \tag{7}$$

we can therefore calculate the ground-state energy per atom in a solid. Comparing this energy with the ground-state energy of an isolated atom which can be computed with the aid of well-known sum rules:

$$(E_0)_{\text{atom}}=-\frac{Ze^2}{\pi}\int_0^{\infty}f(Q)dQ+\frac{e^2}{2\pi}\int_0^{\infty}(I_{\text{tot}}-Z)dQ , \tag{8}$$

where $f(Q)$ is the spherically averaged atomic x-ray-scattering factor and $I_{\text{tot}}$ is the total intensity in e.u., we can, at least in principle, calculate the difference in ground-state energies between one isolated atom and one atom in a solid; that is, the cohesive energy. However, looking at Eq. (5) it is clear that the calculation of total energy implies the inclusion of a very large number of reciprocal-lattice vectors. Indeed, even in the case of a light element such as Be, over 12 000 reciprocal-lattice vectors had to be included in order to have the total energy converged up to the third decimal place. Moreover, interpolations problems appear to have some relevance. Having this in mind it is clear that it is more convenient to treat free atom and solid in the same way. In order to do this we observe that Eq. (8) is composed of two contributions. The first is the classical electrostatic energy of the electronic charge density in the nuclear field, while the second contains the electron-electron repulsive energy and the electronic self-energy. We also have that the contribution due to $S(Q)$ is in the same form of the corresponding term in Eq. (5). To put the electronic energy of the free atom in the same form of the solid we consider $N$ free atoms forming the same lattice of the solid, but with infinitely large lattice parameters. Because of the charge neutrality of each atom we can reduce the volume of this lattice to that of the solid with no change in energy if the atomic charge density is kept constant. It is then clear that we regain Eq. (5) with the structure factors substituted by

$$F^{\text{atom}}_{\vec{G}}=f(G)F^g_{\vec{G}} . \tag{9}$$

The energy difference obtained from the measurement of the scattering factor at $n$ reflections can be easily calculated from the above equations. Supposing for simplicity that all atoms in the unit cell are equivalent, so that Eq. (9) obtains also for the solid, one has

$$\begin{aligned}\Delta E_0 &\propto -Z\left[\sum_i|F^g_i|^2\Delta f_i-\frac{1}{2Z}\sum_i|F^g_i|^2\Delta f_i^2\right]\\ &=-\left[\sum_i\frac{|F^g_i|^2(Z-f_i)\Delta f_i}{G_i^2}-\tfrac{1}{2}\sum_i\frac{|F^g_i|^2(\Delta f_i)^2}{G_i^2}\right]\end{aligned} \tag{10}$$

where the sum runs over the $n$ measured reflections, $f_i$ is the solid atomic scattering factor at the $i$th reflection, and $\Delta f_i$ is the corresponding difference between solid and atom. An obvious consequence of Eq. (10) is that if all $\Delta f_i$'s are nonpositive, then $\Delta E_0$ is non-negative. In the same way total energy differences due to dynamical effects (exchange and correlations) can be calculated from the incoherent scattering cross section.

## RESULTS AND DISCUSSION

A comparison of known values of cohesive energy with energy differences calculated from the formulas of the preceding section allows an assessment of the accuracy and completeness of available experimental and theoretical data. Representative results on Be, Si, Al, and Cu, for all of which extensive calculations and measurements have been carried out, will be presented below.

For atomic calculations the coherent and incoherent scattering cross sections of Be have been obtained by Benesch and Smith[2] from configuration-interaction wave functions, which account for 93% of correlation energy. In the present context, therefore, these cross sections are practically exact. For all other atoms relativistic Hartree-Fock scattering factors[9] and nonrelativistic Hartree-Fock incoherent scattering cross sections[6] have been tabulated. In order to estimate the accuracy of these calculations the total energy of atomic Al and Si ($\sim -7000$ and $-8000$ eV/atom, respectively) have been computed and compared with spectroscopic values (spectroscopic data for Cu are incomplete). Measured and calculated values have been found to differ by 9 eV/atom for Al and 16 eV/atom for Si, with calculated energies lower (more stable) than spectroscopic values. We believe that this result, apparently contradictory with the variational principle, is due to the high $(\sin\theta)/\lambda$ region where tabulated values are very approximate and too coarsely spaced. In any case it might seem that since these differences are much larger than cohesive energies (3—4 eV/atom) no conclusion on the accuracy of experimental cross sections can be reached on the basis of energy-difference calculations. However, since for each solid only a few values of the scattering factor and the incoherent cross section have been measured (all of which in the low-$[(\sin\theta)/\lambda]$ region) the error on energy differences resulting from corresponding free-atom data is only a small part of the error on total energy. This consideration shows that at least on a semiquantitative basis, correct information can be extracted from this type of energy calculations.

Extensive measurements of the scattering factor[10] and the incoherent scattering cross section[5] of crystalline Be have been reported. The energy difference due to the scattering factor is $-0.7$ eV/atom (solid lower) while the difference due to the incoherent scattering cross section is $-3.8$ eV/atom. The resulting cohesive energy of 4.5 eV/atom (taken positive according to current usage) compares well with the thermochemical value of 3.34 eV/atom. We note that the contribution to cohesive energy of exchange and correlations is far from negligible and that its value is consistent with the estimate of 1.4 eV/atom due to correlations alone, recently reported by Dovesi *et al.*[11]

In the case of Si the scattering factor of 15 reflections has been measured by Aldred and Hart[12] from a perfect crystal while the incoherent scattering cross section has been measured by Weinberg[13] and by Paakkari and Suortti[14] up to $(\sin\theta)/\lambda \sim 0.5$ Å$^{-1}$. The energy difference due to the scattering factor is 5 eV/atom (solid higher) including the contribution to the electron-electron repulsive energy given by the *forbidden* (222) reflection, for which a recent measurement by Alkire *et al.*[15] has been used. The energy difference due to the incoherent scattering is $-3.9$ eV/atom, so that the calculated cohesive energy is $-1.1$ eV/atom instead of the thermochemical value of 4.66 eV/atom. Considering that measured cross sections contribute $\sim \frac{1}{3}$ of total energy one has that the error on free-atom values could account for a sizable part of the difference between measured and calculated cohesive energy. Qualitatively one can conclude that measured cross sections are compatible with known cohesive energy. However, in order to really check the claimed 0.1% accuracy on crystal scattering factors, better atomic calculations and a larger set of experimental coherent and incoherent cross sections would be necessary.

The incoherent scattering cross section for Al has been reported by Laval[16] and Walker[17] up to $(\sin\theta)/\lambda \sim 0.6$ Å$^{-1}$, while the scattering factor has been measured, among others, by Raccah and Henrich[18] and Inkinen *et al.*[19] up to $(\sin\theta)/\lambda \sim 0.6$ Å$^{-1}$, with nearly coinciding results. The energy difference due to the incoherent scattering cross section is 0 within the errors, while the difference due to the scattering factor is 11 eV/atom (solid higher), as one could anticipate from the fact that all crystal scattering factors are lower than free atom. A comparison between atomic and solid-state calculations can be made using the band-calculated values reported by Tawil.[20] The band scattering factors are systematically lower than free atom up to $(\sin\theta)/\lambda \sim 0.6$ Å$^{-1}$ with a resulting energy difference of 19 eV/atom. This difference decreases to 12 eV/atom if one uses all published band values $[(\sin\theta)/\lambda \lesssim 0.8$ Å$^{-1}]$. Considering that thermochemical cohesive energy is 3.34 eV/atom, one has that the difference ($\sim 15$ eV/atom) between thermochemical and x-ray-calculated cohesive energies is several times larger than the error introduced in the calculations by the free-atom scattering factor. In order to understand the origin of this difference we have calculated the incoherent scattering cross section of crystalline Al in the slowly-varying-density approximation[5,21] starting from the charge density reported for the solid by Moruzzi *et al.*[22] Comparing crystal and free-atom incoherent scattering cross sections, one has that the contribution to total energy from $S(Q)$ is the same within 1 eV/atom in both cases, in agreement with experiment. Moreover this contribution is only $\sim 250$ eV/atom so that an error of 15 eV/atom in its evaluation is highly unlikely, while a contribution of a few eV as in Be and Si is possible. A clue as the origin of the 15-eV difference is offered by the observation that the difference between band-calculated and free-atom scattering factors reverses its sign at about $(\sin\theta)/\lambda \sim 0.6$ Å$^{-1}$, with the band-calculated scattering factors being still significantly higher than free atom at $(\sin\theta)/\lambda \sim 0.8$ Å$^{-1}$. Admitting that the difference between crystal and free-atom scattering factors has an oscillating trend one would have that the observed difference arises essentially from lack of sufficient experimental values. Of course such a difference might become smaller and smaller for successive oscillations with increasing difficulty or even impossibility of its experimental detection.

The necessity of having accurate values of the scattering factor up to high values of $(\sin\theta)/\lambda$ is indicated also by Cu. The most complete set of scattering factors has been recently obtained by means of $\gamma$-ray diffractometry by Schneider *et al.*[23] The measured crystal values are systematically lower than free-atom values up to

$(\sin\theta)/\lambda \sim 0.8$ Å$^{-1}$, while in the range 0.8 Å$^{-1} \leq (\sin\theta)/\lambda \leq 1.5$Å$^{-1}$, for the reflections which have been measured, they are equal to free-atom values within the errors. For the incoherent scattering cross section no measurement of this quantity is available. The energy difference arising from the scattering factors is $\sim 97$ eV/atom (solid higher) while the cohesive energy of Cu is 3.5 eV/atom. Band-calculated values obtained by Bagayoko are also reported in Ref. 23. These values are systematically lower than free-atom values only up to $(\sin\theta)/\lambda \sim 0.5$ Å$^{-1}$ and, being intermediate between measured crystal values and free-atom calculations, result in an energy difference of 38 eV/atom (solid higher). The contribution to cohesive energy of the incoherent scattering cross section can be calculated following the procedure mentioned for Al. While the contribution to total energy is $\sim 2\%$ (900 out of 45 000 eV/atom) the difference between solid and free-atom values is less than 1 eV/atom. Although this result is probably in error by approximately 1% or 2% of 900 eV/atom, it shows nonetheless that the incoherent scattering cross section cannot account for the 100 eV/atom due to the scattering factors. Of course this remark and the corresponding one made for Al are not in contrast with the previous observation that the energy difference due to the incoherent scattering cross section may be crucial for determining cohesion, as this phenomenon is due to energy differences of the order of a few eV/atom. It is also clear that errors in the calculation of the free-atom scattering factor cannot be responsible for the observed discrepancy since this would amount to lowering free-atom values by an amount ranging from 2.5% at $(\sin\theta)/\lambda \sim 0.25$ Å$^{-1}$ to zero at $(\sin\theta)/\lambda \sim 0.8$ Å$^{-1}$. This is inconsistent with the fact that different atomic calculations[24,25] yield the same scattering factor to better than 0.5% up to $(\sin\theta)/\lambda \sim 1$ Å$^{-1}$. All these facts suggest that the 100-eV/atom discrepancy is likely to arise from a combination of the following: (1) the crystal scattering factor becomes larger than free atom at high values of $(\sin\theta)/\lambda$. For instance, the correct value of cohesive energy would be obtained if crystal values were higher than free atom by $0.1e$ for $(\sin\theta)/\lambda$ between 0.8 and 1.6 Å$^{-1}$. Such a difference is at the limit of experimental accuracy and, of course, is just an example of the order of magnitude of required differences; (2) the measured scattering factors are too low because of some systematic error, as suggested by the fact that the scattering factor for the (111) and (200) reflections obtained from critical voltage measurements[26,27] are in agreement with band-theoretical values and differ significantly from $\gamma$-ray results.

From all above data it appears that in order to derive cohesive energies from scattering cross sections it is necessary to perform very accurate measurements up to rather high values of $(\sin\theta)/\lambda$. Such measurements are probably at the limit of present possibilities. Also, a significant check on band-calculated scattering cross sections could be performed if theorists would calculate these quantities up to the point where differences from free-atom values become negligible.

A final remark concerns the suggestion by Weiss and Mazzone[3] that scattering factors should be measured at small values of $(\sin\vartheta)/\lambda$ by examining the thermal diffuse scattering. This suggestion originated from the recognition that since measured scattering factors tend to be lower than those of the free atom, a possible contribution to cohesion would arise if the crystal scattering factor was higher than that of the free atom in the low-$[(\sin\vartheta)/\lambda]$ region. This suggestion, consistent with the approximate treatment of the relation between scattering and cohesion reported in Ref. 3, turns out to be incorrect in the light of present work which shows that the total energy of a crystal depends only on the value of the scattering factor at reciprocal-lattice nodes.

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