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Self-consistently determined properties of solids without band-structure calculations

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We propose an approach to the calculation of the cohesive and the structural properties of solids. This approach is based on the second theorem of Hohenberg and Kohn and allows one to obtain directly the charge density and the total energy without determining, at the same time, the band structure of the system. The method is easy to implement, is self-consistent, and suggests a meaning for concepts such as "atoms in solids," "crystalline field," and "charge transfer," which are not, in general, well defined in the context of *ab initio* calculations. The results of applications to some alkali halide crystals are compared with the corresponding results obtained by several authors using traditional techniques for band-structure calculations.

The density-functional theory (DFT) is based on the two Hohenberg-Kohn (HK) theorems.[1] The first of these theorems states the existence of a one-to-one correspondence between the ground-state charge density of an N-electron system and the external potential acting on it. A major consequence of this is that the total energy of the system is a universal functional of the ground-state charge density:

$$E[\rho]=F[\rho]+\int V[\rho]\rho\, d^3r \ . \tag{1}$$

The second HK theorem states that the exact charge density of the system can be found by replacing $V[\rho]$ in Eq. (1) with the external potential $V_{\text{ext}}(\mathbf{r})$ and then looking for the absolute minimum of the resulting functional $E_v[\rho]$:

$$\begin{aligned} E_v[\rho]&=F[\rho]+\int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r \\ &=T_i[\rho]+V_{ee}[\rho]+\int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r \ . \end{aligned} \tag{2}$$

In Eq. (2), the functional $F[\rho]$ has been separated into two terms: the kinetic energy of the electrons, $T_i[\rho]$, and their interaction energy, $V_{ee}[\rho]$.

The usual method for determining the ground-state charge density ρ is due to Kohn and Sham[2] and is the following. One assumes the existence of a noninteracting electron system having the same ground-state charge density as the interacting system. Indicating with $T_{\text{ni}}[\rho]$ the kinetic energy of the noninteracting system[3] and with $J[\rho]$ the electrostatic energy of the electrons, Eq. (2) becomes

$$E_v[\rho]=T_{\text{ni}}[\rho]+J[\rho]+E_{\text{xc}}[\rho]+\int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r \ , \tag{3}$$

where $E_{\text{xc}}[\rho]$ is the exchange-correlation functional defined by

$$E_{\text{xc}}[\rho]=T_i[\rho]-T_{\text{ni}}[\rho]+V_{ee}[\rho]-J[\rho] \ . \tag{4}$$

The N-electron charge densities which make Eq. (3) stationary are then the solutions of the equation

$$\frac{\delta T_{\text{ni}}}{\delta\rho}+\frac{\delta J}{\delta\rho}+\frac{\delta E_{\text{xc}}}{\delta\rho}+V_{\text{ext}}=\mu \ . \tag{5}$$

Since Eq. (5) is identical to the equation that would be obtained for a noninteracting system in an external effective potential given by

$$V_{\text{eff}}(\mathbf{r})=V_{\text{ext}}(\mathbf{r})+\frac{\delta J}{\delta\rho}+\frac{\delta E_{\text{xc}}}{\delta\rho} \ , \tag{6}$$

and since for this latter system one knows that the ground-state charge density can be obtained by solving the Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+v_{\text{eff}}(\mathbf{r})]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r}) \ , \tag{7}$$

and then summing the square of the N lowest orbitals

$$\rho(\mathbf{r})=\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2 \ , \tag{8}$$

one has a practical tool to perform electronic structure calculations.

The wave functions which enter in Eq. (7) are wave functions for the overall system. Thus, in the solid-state case, the solution of Eq. (7) gives rise to a usual band-structure problem and the following steps depend strictly on the method one wishes to use for solving it. In particular, one chooses a basis set to expand the wave functions. Since it is not possible to use complete basis sets, this is equivalent, in practice, to restricting the wave functions to have a given expression. The first basic idea of the method proposed in this paper is to do a similar approximation, but some steps before, namely in Eq. (3).

Let us consider a nonmagnetic crystal and indicate with $\mathbf{R}_k$ the lattice points. We will use τ_j to indicate some point within a unitary cell (the positions of the atoms of the basis of the crystal and, in some cases, some other point). We associate to each point $\mathbf{R}_k+\tau_j$ an atomiclike charge density

$$\rho_j(\mathbf{r}-\mathbf{R}_k-\tau_j)=\sum_i 2n_{ij}|\psi_{ij}(\mathbf{r}-\mathbf{R}_k-\tau_j)|^2 \ , \tag{9}$$

where the coefficients n_{ij} are fermionic occupation numbers, and the wave functions ψ_{ij} are normalized and are supposed to satisfy the usual boundary conditions for atomic orbitals. Accordingly, we will speak, in the following, of "atoms" even if a positive nucleus does not necessarily correspond to each site. We write the total charge density of the crystal as

$$\rho_{\text{tot}}(\mathbf{r})=\sum_{j,k}\rho_j(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j)=\sum_{j,k}\rho_{jk} \ . \tag{10}$$

We will look for the minimum of $E_v[\rho]$ limiting the search to charge densities of the form given in Eqs. (9) and (10). In an equivalent way, it is also possible to consider E_v as a functional of ψ_{ij} and to perform a general variation of E_v by independently varying the ψ_{ij}.

Let us associate now to each atom a kinetic energy defined by

$$T_a[\psi_{ij}]=\sum_i 2n_{ij}\langle\psi_{ij}|-\tfrac{1}{2}\nabla^2|\psi_{ij}\rangle \ . \tag{11}$$

Using this definition, the kinetic energy of Eq. (3) can be separated in an intra-atomic and an interatomic contribution by writing the identity

$$T_{\text{ni}}[\rho]=\sum_{j,k}T_a[\psi_{ij}]+\left[T_{\text{ni}}[\rho]-\sum_{j,k}T_a[\psi_{ij}]\right] \ . \tag{12}$$

The second key point of the method is to treat the intra-atomic kinetic energy exactly and to use some kind of approximation for the interatomic kinetic energy. To be more explicit, let us suppose to have an approximate expression $T^{\text{approx}}[\rho]$ of the functional $T_{\text{ni}}[\rho]$. Then, we will write

$$E_v^{\text{approx}}[\psi_{ij}]=\sum_{j,k}T_a[\psi_{ij}]+\left[T^{\text{approx}}[\rho]-\sum_{j,k}T^{\text{approx}}[\rho_{jk}]\right]+J[\rho]+E_{\text{xc}}^{\text{approx}}[\rho]+\int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r \ , \tag{13}$$

where we have made explicit the fact that also $E_{\text{xc}}[\rho]$ will be approximate. If we now perform a variation of $E_v^{\text{approx}}[\psi_{ij}]$, under the normalization condition for the ψ_{ij}, and for a fixed choice of n_{ij}, we obtain the following stationarity condition:

$$\left[-\frac{1}{2}\nabla^2+V_{\text{ext}}+\frac{\delta J}{\delta\rho}+\frac{\delta E_{\text{xc}}^{\text{approx}}}{\delta\rho}+\frac{\delta T^{\text{approx}}}{\delta\rho}-\frac{\delta T^{\text{approx}}}{\delta\rho_{jk}}\right]\psi_{ij}(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j)=\varepsilon_{ij}\psi_{ij}(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j) \ . \tag{14}$$

This is a Schrödinger equation for each atom in the crystal. However, because of the translational symmetry, it is only necessary to solve for the atoms in one unitary cell, for example, the cell corresponding to $\mathbf{R}_k=0$. Furthermore, the expression of the potential entering in Eq. (14) can be written in a form which is more practical for the calculations and, at the same time, more appealing from a physical standpoint. Considering the electrostatic part of the potential

$$V_{\text{ext}}+\frac{\delta J}{\delta\rho}=\sum_{j,k}\left[-\frac{Z_j}{|\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j|}+\int\frac{\rho_j(\mathbf{r}'-\mathbf{R}_k-\boldsymbol{\tau}_j)}{|\mathbf{r}-\mathbf{r}'|}d^3r'\right] , \tag{15}$$

and introducing the ionic charges I_j of the atoms, we can write

$$V_{\text{ext}}+\frac{\delta J}{\delta\rho}=-\sum_{j,k}\frac{I_j}{|\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j|}+\sum_{j,k}\left[-\frac{Z_j-I_j}{|\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j|}+\int\frac{\rho_j(\mathbf{r}'-\mathbf{R}_k-\boldsymbol{\tau}_j)}{|\mathbf{r}-\mathbf{r}'|}d^3r'\right] . \tag{16}$$

The first term on the right-hand side of this equation is a point-ion contribution and it can be summed by standard techniques. The second term is a short-range term. Hence, it is not necessary to perform the sum on all the lattice vectors of the crystal: Only a few orders of neighbors give a non-negligible contribution to the potential in the points where the electronic density of a given atom is not too small. This latter fact is also true for the exchange-correlation and for the kinetic contributions to the potential. Thus, in explicitly calculating the potential to be used in Eq. (14) for a given atom, one has to perform a sum on all the lattice vectors of the crystal just for the point-ion contribution.

Finally, it is possible to separate the potential acting on each atom in an intra-atomic term and a crystalline potential V_{cryst}. To do this it is sufficient to use the identity

$$\frac{\delta E_{\text{xc}}}{\delta\rho}=\frac{\delta E_{\text{xc}}}{\delta\rho_{jk}}+\frac{\delta E_{\text{xc}}}{\delta\rho}-\frac{\delta E_{\text{xc}}}{\delta\rho_{jk}} , \tag{17}$$

and to separate, in the Coulombic potential [Eq. (16)], the internal contributions from those coming from the other atoms.

Thus, the problem of determining the charge density of a crystal has been reduced to the calculation of the charge densities of single atoms in a crystalline potential. Of course, V_{cryst} has to be self-consistently determined in the calculation.

In order to complete the description of the method, we only need to discuss how to determine the occupation numbers n_{ij}. From the discussion above, the "correct" n_{ij} are those which minimize the total energy given in Eq. (13). These n_{ij} can be found by filling up the levels of the atoms in the unitary cell following the Fermi statistics. The proof of this follows immediately from the fact that the eigenvalues ε_{ij} of Eq. (14) are proportional to the partial derivative of the total energy of the system with respect to n_{ij}. The explicit form of this proportionality can be established in the same way as it was done by

Janak[4] to prove the analogous result for the Kohn-Sham eigenvalues. We repeat here his proof because, in our case, the ε_{ij} *are not* the eigenvalues of the overall system. Thus our Eq. (23) is not an obvious consequence of the Janak work.

Consider the total energy $E_v^{\text{approx}}[n_{ij},\psi_{ij}]$ given in Eq. (13) and indicate the sum of the functionals of ρ contained in it with $G[\rho]$. The partial derivative of $G[\rho]$ with respect to n_{ij} is given by [we will indicate $\psi_{ij}(\mathbf{r}-\mathbf{R}_k-\tau_j)$ with ψ_{ijk}, T^{approx} with T, and E_v^{approx} with E]

$$\frac{\partial G}{\partial n_{ij}}=\int\frac{\delta G}{\delta\rho}\sum_k\left[2|\psi_{ijk}|^2+\sum_{i',j'}2n_{i'j'}\frac{\partial}{\partial n_{ij}}|\psi_{i'j'k}|^2\right]d^3r\ . \tag{18}$$

Furthermore, for the remaining terms on the right-hand side of Eq. (13), we have

$$\frac{\partial}{\partial n_{ij}}\sum_{j',k}T[\rho_{j'k}]=\sum_k\int\left[\frac{\delta T}{\delta\rho_{jk}}2|\psi_{ijk}|^2+\sum_{i',j'}\frac{\delta T}{\delta\rho_{j'k}}2n_{i'j'}\frac{\partial}{\partial n_{ij}}|\psi_{i'j'k}|^2\right]d^3r \tag{19}$$

and

$$\frac{\partial}{\partial n_{ij}}\sum_{i',j',k}2n_{i'j'}\langle\psi_{i'j'k}|-\tfrac{1}{2}\nabla^2|\psi_{i'j'k}\rangle=\sum_k2\langle\psi_{ijk}|-\tfrac{1}{2}\nabla^2|\psi_{ijk}\rangle+\sum_{i',j',k}\left[2n_{i'j'}\left\langle\frac{\partial\psi_{i'j'k}}{\partial n_{ij}}\right|-\tfrac{1}{2}\nabla^2\left|\psi_{i'j'k}\right\rangle+\text{c.c.}\right]\ . \tag{20}$$

Summing up the second terms on the right-hand side of Eqs. (18) and (20) and substracting the corresponding term of Eq. (19), we obtain

$$\sum_{i',j',k}2n_{i'j'}\varepsilon_{i'j'}\frac{\partial}{\partial n_{i'j'}}\int|\psi_{i'j'k}|^2d^3r=0\ , \tag{21}$$

where we have used Eq. (14) and where the equality to zero follows from the normalization condition for the orbitals. Thus the result is

$$\frac{\partial E}{\partial n_{ij}}=\sum_k\left[\int\left[\frac{\delta G}{\delta\rho}+\frac{\delta T}{\delta\rho_{jk}}\right]2|\psi_{ijk}|^2d^3r+2\langle\psi_{ijk}|-\tfrac{1}{2}\nabla^2|\psi_{ijk}\rangle\right]=\sum_k2\varepsilon_{ij}\ , \tag{22}$$

which is equivalent to writing

$$\varepsilon_{ij}=\frac{1}{2}\frac{1}{N_c}\frac{\partial E}{\partial n_{ij}}\ , \tag{23}$$

where N_c is the total number of unitary cells in the crystal, and the factor $\frac{1}{2}$ derives from the fact that we are in the non-spin-polarized case.

Before discussing the first results obtained by the method described above, two further points need to be considered. First, one has to choose an approximate expression for the exchange-correlation and for the interatomic kinetic energy. Following a successful tradition in DFT, it seems natural to test, at first, the local-density approximation for both contributions. Thus, we have used the two classical expressions

$$T^{\text{approx}}=\tfrac{3}{10}(3\pi^2)^{2/3}\int\rho^{5/3}(\mathbf{r})d^3r \tag{24}$$

and

$$E_x^{\text{approx}}=-\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3}\int\rho^{4/3}(\mathbf{r})d^3r \tag{25}$$

for the kinetic and for the exchange energy, respectively, while, for the correlation, we have taken the expression derived by Perdew and Zunger[5] from the Ceperley-Alder[6] Monte Carlo calculations for the homogeneous gas.

Second, in order to simplify the calculations, we have further restricted the class of the possible total charge density of the crystal. In fact, we have only considered superpositions of spherically symmetric atomic charge density ρ_j. Since ρ_j is determined by solving a Schrödinger equation containing the crystal field, this restriction implies that some kind of spherical average of the latter has to be performed. There are two nonequivalent ways of getting a spherical potential. In the first one, the full nonspherical potential is calculated and then the spherical average of it is performed; in the second one, the charge density from which the potential is derived is spherically averaged. In our opinion, there is no particular reason to prefer one of these two methods to the other. The latter is more commonly used and is certainly easier to implement. For these two reasons we have chosen this "averaged-density approximation" for our calculations.

From the standpoint of applications, one expects the method we have described to give the best results for systems with localized valence electrons: ionic, covalent, and molecular systems. In a first attempt of verifying the capability of our method to predict the physical properties of crystals, we have performed a few calculations for alkali-halide solids. We report here the results for the prototype of these solids, the NaCl, for which the comparison with several different band-structure calculations is possible. In particular, this system has been studied by Williams, Kübler, and Gelatt[7] (WKG), by the

TABLE I. Lattice parameter a, bulk modulus B, and cohesive energy E_c of NaCl. Expt, experimental data (Refs. 11–13); WKG, augmented-spherical-wave calculations (Ref. 7); AMS and FC, first-principle pseudopotentials (Refs. 8 and 9); JF, full-potential linearized augmented-plane-wave results (Ref. 10).

	Expt	WKG	AMS	FC	JF	Present
a (Å)	5.60	5.40	5.28	5.52	5.64	5.75
B (GPa)	26.6	32.0	24.0	31.2	30.4	23.2
E_c (eV)	6.39	6.57			6.61	6.32

augmented-spherical-wave (ASW) method, by Andreoni, Maschke, and Schlüter[8] (AMS) and by Froyen and Cohen[9] (FC), using first-principles pseudopotentials, and by Jansen and Freeman[10] (JF), by the full-potential linearized-augmented-plane-wave method.

The results obtained by these authors for the lattice parameter, the bulk modulus, and the cohesive energy are reported in Table I, together with our own results and the corresponding experimental data. Note that we have taken into account the short-range contributions to the potential till the fourth order of neighbors. Beyond this order, the ions have been considered as point charges. Without overemphasizing the comparison between the various methods, we only wish to remark that our results are as accurate as those obtained by band-structure calculations. Incidentally, we have found the charge transfer from sodium to chlorine to be exactly one electron.

The other question we have addressed is the relative stability of the NaCl phase ($B1$) with respect to the CsCl phase ($B2$) for the NaCl crystal. It is well known that to find the correct crystallographic phase is not an easy problem for *ab initio* calculations. For example, the ASW method gives the $B2$ phase more stable than the $B1$ (Ref. 14) phase. On the contrary, we find the correct crystallographic phase. Furthermore, the difference between the minima of the total energy curves as function of the lattice parameter corresponding to the two phases is 9 mHartree, which agrees with the value of about 10 mHartree, estimated from Fig. 1 of the FC paper. We have also evaluated the pressure required to induce the phase transition $B1 \rightarrow B2$. We have found 11 GPa, which is smaller than the experimental value[15] (30 GPa) by a factor about 3.

TABLE II. Structure factors at 295 K for KCl. Expt, experimental data (Ref. 16); ASW, augmented-spherical-wave calculations (Ref. 18).

hkl	Expt	ASW	Present
111	1.33	1.33	1.34
220	22.05	21.89	21.99
222	18.55	18.60	18.64
400	15.80	16.25	16.25
422	12.87	13.02	13.00
442	9.92	9.97	9.97
600	9.65	9.97	9.97
444	7.80	7.93	7.93
800	5.90	5.97	5.98
1000	3.22	3.25	3.25

Finally, we have studied the effects of the crystalline field on the electronic charge density by calculating the structure factors for KCl. We have decided to examine KCl rather than NaCl for two reasons. First, for NaCl accurate experimental data are not available, while for KCl there are the recent γ-ray measurements by Schmidt, Colella, and Yoder-Short.[16] Second, KCl is an "isoelectronic" salt and this implies that the lower-order odd reflections have small intensities and are strongly affected by the crystal field.[17]

In Table II we compare our calculated structure factors with those obtained by Böbel, Cortona, and Fumi[18] using the ASW method and with the experimental results. The thermal effects have been taken into account by using the Debye-Waller factors reported by Reid and Smith.[19] It can be seen that the three sets of values agree very well: The discrepancies between theoretical and experimental results are contained within a few percent, while ASW and the method of the present paper agree within 1%.

In conclusion, the results reported above seem to indicate that the method of the present paper can be used to determine with a good degree of accuracy the cohesive and the structural properties of solids (at least in the case of ionic crystals). This is still more remarkable considering the relative simplicity of the method with respect to the band-structure calculations.

From a technical standpoint, one has only to take care in choosing the mesh to perform the integration of Eq. (14): In correspondence to the various orders of neighbors there are strong variations of the potential which must be accurately taken into account.

Several improvements of the calculations presented here can be considered: Nonspherical effects can be included and nonlocal functionals for the interatomic kinetic and for the exchange-correlation energies can be used. In particular, the self-interaction correction, which in solid-state calculations generally requires very complicated techniques,[20,21] can be implemented quite directly. We believe that this is a non-negligible advantage of our method.

Finally, in spite of the fact that we have discussed the case of solids, the theory of this paper can also be applied without modifications to molecules. Of course, for the latter (as well as for very anisotropic solids), taking into account the nonspherical effects can be crucial in order to obtain accurate results.

A method to avoid the solution of the Kohn and Sham equation and to get directly to the charge density of the system has also been proposed by Yang[22] in a recently published paper. The basic idea of partitioning the overall system in localized subsystems is also used in the Yang work, but the way of obtaining the charge density of the system is different. A careful comparison between the two methods can be quite useful.

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[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[3] There are a few different ways of introducing the functional $T_{\mathrm{ni}}[\rho]$. We refer to R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989), and references therein, for a discussion of this point as well as for a complete review of the DFT.

[4] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).

[5] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[6] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[7] A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. B **19**, 6094 (1979).

[8] W. Andreoni, K. Maschke, and M. Schlüter, Phys. Rev. B **26**, 2314 (1982).

[9] S. Froyen and M. L. Cohen, Phys. Rev. B **29**, 3770 (1984).

[10] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **33**, 8629 (1986).

[11] W. Pies and A. Weiss, in *Crystal Structure Data of Inorganic Compounds*, edited by K. H. Hellwege and A. M. Hellwege, Landolt-Börnstein, New Series, Group **III**, Vol. 7, Pt. a (Springer-Verlag, New York, 1973).

[12] J. T. Lewis, A. Lehoczky, and C. V. Briscoe, Phys. Rev. **161**, 877 (1967).

[13] Experimental cohesive energy reported in Ref. 10.

[14] Reference 7, footnote 63.

[15] W. A. Bassett, T. Takahashi, H. K. Mao, and J. S. Weaver, J. Appl. Phys. **39**, 319 (1968).

[16] M. C. Schmidt, R. Colella, and D. R. Yoder-Short, Acta Crystallogr. Sec. A **41**, 171 (1985).

[17] R. J. Elliott and A. F. Gibson, *An Introduction to Solid State Physics* (Macmillan, New York, 1974).

[18] G. Böbel, P. Cortona, and F. G. Fumi, Acta Crystallogr. Sec. A **45**, 112 (1989).

[19] J. S. Reid and T. Smith, J. Phys. Chem. Solids **31**, 2689 (1970). The Debye-Waller factors reported in this paper are theoretical values calculated from experimental phonon dispersion curves. See also Ref. 18 for a critical discussion of the use of the Debye-Waller factors for alkali halides.

[20] R. A. Heaton, J. G. Harrison, and C. C. Lin, Phys. Rev. B **28**, 5992 (1983).

[21] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).

[22] W. Yang, Phys. Rev. Lett. **66**, 1438 (1991).