Structure constants in the Green's-function method: A new analytic evaluation

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A new efficient procedure to calculate the structure constants in the Green's-function method is presented. The conventional algorithm in terms of the Ewald sums is replaced by alternate and quite convenient analytic expressions. As a specific test the conduction bands of solid neon are obtained. The relationship with the Segall-Yang approach is discussed.

I. INTRODUCTION

The Green's function method [or Korringa-Kohn-Rostoker (KKR) method[1]] has found wide applications in the study of electronic properties of materials. The multiple-scattering approach is very appealing from a formal point of view because it provides the same unified basis to discuss apparently different problems. The method has been successfully employed to study perfect bulk crystals (see, for instance, Refs. 2–4), electromagnetic propagation in heterogeneous media,[5] impurities,[6] clusters,[7] thin films and surfaces,[8] alloys,[9] etc.; the method has also fostered parallel techniques based on linear combinations of muffin-tin orbitals.[10]

Among the procedures for band-structure calculations,[11] the KKR method is one of the most powerful tools. Its advantages with respect to other cellular methods can be summarized as follows: (i) sharp and elegant separation of the problem of electronic state calculations into two parts, namely (a) scattering properties (phase shifts) of the muffin-tin potential and (b) structural aspects of the lattice; (ii) no explicit dependence of the choice of muffin-tin radii; (iii) very rapid convergence.

These important advantages are to some extent counterbalanced by the computational difficulties connected with the evaluation and storage of the structure coefficients $D_{LM}(E,\vec{k})$, which depend on the energy E and wave vector $\vec{k}$. In the last two decades the standard method for their evaluation has been the Ewald partition.[12] This procedure is rather laborious when repeated in a sufficiently fine mesh in the Brillouin zone and in the energy variable, and constitutes the most delicate aspect of the formalism (see, for instance, Refs. 2–4, 13, and 14, and references quoted therein).

The presence of the poles in the structure constants at the empty-lattice eigenvalues is the basis of attempts to separate the singular part from the smooth part. Consider, for instance, the expression of $D_{00}(E,\vec{k})$ in the form

$$D_{00}(E,\vec{k})=\frac{\sqrt{4\pi}}{\Omega}\sum_{\vec{k}_n}\frac{1}{E-k_n^2}+\frac{\sqrt{E}}{\sqrt{4\pi}}\lim_{r\to 0}\cot(\sqrt{E}r)\ , \tag{1}$$

where $\vec{k}_n=\vec{k}+\vec{h}_n$, $\vec{h}_n$ are the reciprocal-lattice vectors and Ω is the unit-cell volume. To obtain the effective mass at $\vec{k}=0$ in the nearly-free-electron case, Ziman[15] extracted from Eq. (1) only the singular term corresponding to $\vec{h}_n=0$.

To give a better justification of Ziman's procedure, in particular, his neglect of the divergent term of the type $1/r$ for $r\to 0$, the present authors have implemented the Ziman procedure with the following analytic approximation of Eq. (1):

$$D_{00}(E,\vec{k})\cong\frac{\sqrt{4\pi}}{\Omega}\sum_{k_n<k_c}\frac{1}{E-k_n^2}+\frac{k_s}{\pi^{3/2}}-\frac{\sqrt{E}}{2\pi^{3/2}}\ln\frac{k_s+\sqrt{E}}{k_s-\sqrt{E}}\ . \tag{2}$$

In Eq. (2) k_c is a chosen cutoff value and k_s is the radius of a sphere such that

$$\tfrac{4}{3}\pi k_s^3=m\Omega_{\mathrm{BZ}}\ ,$$

m being the number of k_n vectors smaller than k_c and Ω_{BZ} the volume of the Brillouin zone. The last two terms on the right-hand side of Eq. (2) result from Eq. (1) through the following procedures: (i) replacement of the discrete sum for $k_n\geq k_c$ with a continuous integral provided $E<k_c^2$, and (ii) use of

the identity

$$\frac{1}{r}=\frac{1}{2\pi^2}\int\frac{1}{k^2}e^{i\vec{k}\cdot\vec{r}}d\vec{k}\ . \tag{3}$$

in the limit of $r\to 0$.

More recently, the growing use of the Green's-function method and its extension to several areas of research have stimulated renewed interest (see, for instance, Refs. 4 and 14, and references quoted therein) in the key ingredient of the method: the evaluation of the reduced structure constants. A significant reexamination of this problem was given by Segall and Yang.[4] These authors showed the convenience of separating the singular part of $D_{LM}(E,\vec{k})$ from the smooth part, up to a given energy; the smooth part is then expanded in series with the help of the Ewald algorithm. An analogous separation had earlier been suggested by Williams *et al.*[14] within a similar context. These procedures, however, do not avoid the Ewald algorithm, although they do reduce its use, with some advantages in computational labor.

The purpose of this paper is to present an alternative and efficient procedure for the evaluation of the structure coefficients. In Sec. II we present the new method; the novelty of our procedure is that closed analytic expressions are provided. Both simple lattices and composite lattices are considered. The relationship with the Segall-Yang approach is also discussed. In Sec. III, as a test of the new procedure, we consider the specific case of the conduction bands of solid neon in the Hartree-Fock limit. By utilizing phase shifts from electron-atom scattering experiments, we also estimate the correlation-polarization effects. Section IV contains the conclusion. Some aspects of more mathematical and technical nature are reported in the Appendix.

II. NEW PROCEDURE FOR EVALUATING THE STRUCTURE CONSTANTS

A. General considerations

In this section we briefly summarize the expressions for the structure constants in the extreme limits of summations either in coordinate space or in reciprocal space. It is well known that the use of one of the two spaces requires an impossibly large number of terms in the sum; however, by an appropriate partition between the two spaces it is possible to find an efficient procedure that is an alternative to the Ewald procedure. For simplicity we confine our attention to simple lattices; atomic units are used throughout the paper.

The structure constants $D_{LM}(E,\vec{k})$ for a given energy E and wave vector $\vec{k}$ can be represented as a sum over the reciprocal-lattice vectors in the form

$$D_{LM}(E,\vec{k})=\frac{4\pi}{\Omega}\frac{1}{(\sqrt{E})^L}\sum_{\vec{k}_n}\frac{k_n^L}{E-k_n^2}Y_{LM}(\vec{k}_n)+\frac{1}{\sqrt{4\pi}}\delta_{L0}\lim_{r\to 0}\frac{1}{r}\ , \tag{4}$$

where Y_{LM} are spherical harmonics (or appropriate combinations) in real form. The significance of the symbol $\lim(1/r)$ for $r\to 0$ has been already clarified in our discussion of Eqs. (1)–(3).

Expression (4) is valid both for positive and negative energies. It exhibits poles at the positive values of E corresponding to the empty-lattice eigenvalues. For any energy E the sum (4) is slowly (conditionally) convergent and completely useless for practical calculations.

The structure constants $D_{LM}(E,\vec{k})$ can be represented as a sum over the direct-lattice vectors

$$D_{LM}(E,\vec{k})=i^{-L}\sqrt{E}\sum_{\vec{r}_n\neq 0}e^{i\vec{k}\cdot\vec{r}_n}[n_L(\sqrt{E}\,r_n)-ij_L(\sqrt{E}\,r_n)]Y_{LM}(\vec{r}_n)-\frac{i}{\sqrt{4\pi}}\sqrt{E}\,\delta_{L0}\ , \tag{5}$$

where j_L and n_L are the spherical Bessel and Neumann functions.

In the case of negative E, the direct-lattice sum (5) converges exponentially fast and is thus of interest. However, for positive E (which is the situation of practical relevance) the sum becomes slowly conditionally convergent and completely useless for actual calculations. For positive E, the direct-lattice sum appears to be even worse (from the convergent point of view) than the reciprocal-lattice sum, because it does not exhibit explicitly the expected singularities at the empty-lattice eigenvalues.

B. Ewald algorithm

The standard manner for achieving satisfactory accuracy in the evaluation of the structure constants is the application of the full Ewald algorithm with summations both in direct and reciprocal spaces. For convenience we quote the final expressions[2] in the case of one atom per unit cell:

$$D_{LM}(E,\vec{k})=D_{LM}^{(1)}(E,\vec{k})+D_{LM}^{(2)}(E,\vec{k})+D_{00}^{(3)}(E)\delta_{L0}\ , \tag{6}$$

where

$$D_{LM}^{(1)}(E,\vec{k})=\frac{4\pi}{\Omega}\frac{e^{E/\eta}}{(\sqrt{E})^L}\sum_{\vec{k}_n}\frac{k_n^L e^{-k_n^2/\eta}}{E-k_n^2}Y_{LM}(\vec{k}_n)\ , \tag{7a}$$

$$D_{LM}^{(2)}(E,\vec{k})=\frac{(-2)^{L+1}i^L}{\sqrt{\pi}(\sqrt{E})^L}\sum_{\vec{\tau}_n\neq 0}\tau_n^L e^{i\vec{k}\cdot\vec{\tau}_n}Y_{LM}(\vec{\tau}_n)\int_{\sqrt{\eta}/2}^{\infty}\xi^{2L}\exp\left[-\xi^2\tau_n^2+\frac{E}{4\xi^2}\right]d\xi\ , \tag{7b}$$

$$D_{00}^{(3)}(E)=-\frac{\eta^{1/2}}{2\pi}\sum_{s=0}^{\infty}\frac{(E/\eta)^s}{s!(2s-1)}\ . \tag{7c}$$

The parameter η is arbitrary and is chosen to optimize simultaneously the convergence of the summations in both spaces. The labor involved in the computation of expressions (7) at the desired values of E and $\vec{k}$ is the most time-consuming part in setting up the KKR secular determinant.

An analytic implementation of the Ewald method has been provided by Davis[13] in terms of the incomplete Γ function.[16] Equation (7b) can be rewritten in the form

$$D_{LM}^{(2)}(E,\vec{k})=\frac{-(-2)^L i^L}{\sqrt{\pi}(\sqrt{E})^L}\sum_{m=0}^{\infty}(\tfrac{1}{4}E)^m\frac{1}{m!}\sum_{\vec{\tau}_n\neq 0}\frac{1}{\tau_n^{L-2m+1}}e^{i\vec{k}\cdot\vec{\tau}_n}Y_{LM}(\vec{\tau}_n)\Gamma(L-m+\tfrac{1}{2},\tfrac{1}{4}\eta\tau_n^2) \tag{7b'}$$

and the incomplete Γ function can be calculated using a continued-fraction expansion.

C. A new efficient algorithm

In this section we provide an alternative algorithm for the evaluation of the reduced structure constants; summations in direct and reciprocal spaces are combined in a new feature, which leads to quite convenient analytic expressions. We illustrate the guidelines of the procedure, and summarize the final results, referring the reader to the Appendix for aspects of a more mathematical and technical nature.

Consider in Eq. (4) the term $(k_n^2-E)^{-1}$. If the energy E is negative (say $-E_0$, $E_0>0$) the summation (4) can be conveniently replaced by Eq. (5), which is absolutely convergent in this case. Also note that the denominator $(k_n^2-E)^{-1}$ for large k_n goes as k_n^{-2}, while the difference

$$(k_n^2-E)^{-1}-(k_n^2+E_0)^{-1}$$

$$\equiv(E+E_0)(k_n^2-E)^{-1}(k_n^2+E_0)^{-1} \tag{8}$$

for large k_n goes as k_n^{-4}. Our procedure consists essentially of splitting $(k_n^2-E)^{-1}$ as indicated in (8), iterating it a convenient number of times (say I_0), and utilizing the summation in direct space for the first term and the summation in reciprocal space for the other, both summations being now absolutely convergent.

The details are given in the Appendix. For simple lattices, we report the final expressions in the familiar form

$$D_{LM}(E,\vec{k})=D_{LM}^{(1)}(E,\vec{k})$$

$$+D_{LM}^{(2)}(E,\vec{k})+D_{00}^{(3)}(E)\delta_{L0}\ , \tag{9}$$

where now

$$D_{LM}^{(1)}(E,\vec{k})=\frac{4\pi}{\Omega}\frac{(E+E_0)^{I_0}}{(\sqrt{E})^L}\sum_{\vec{k}_n}\frac{k_n^L}{(E-k_n^2)(E_0+k_n^2)^{I_0}}Y_{LM}(\vec{k}_n)\ , \tag{10a}$$

$$D_{LM}^{(2)}(E,\vec{k})=\frac{1}{(\sqrt{E})^L}\sum_{I=0}^{I_0-1}\frac{(-i)^I}{I!2^I}(E+E_0)^I\sum_{\vec{\tau}_n\neq 0}\tau_n^I e^{i\vec{k}\cdot\vec{\tau}_n}Y_{LM}(\vec{\tau}_n)(\sqrt{E_0})^{L-I+1}h_{L-I}(i\sqrt{E_0}\tau_n)\ , \tag{10b}$$

$$D_{00}^{(3)}(E)=-\frac{2}{3}\frac{\sqrt{E_0}}{\sqrt{4\pi}}\sum_{I=0}^{I_0-1}\frac{(E+E_0)^I}{I!E_0^I}(I-\tfrac{3}{2})(I-\tfrac{5}{2})\cdots(-\tfrac{3}{2})\ . \tag{10c}$$

The simplicity and advantages of the new equations (10) with respect to Eqs. (7) are evident. Further simplifications for computational purposes are discussed in the Appendix. It is worthwhile to emphasize that our Eq. (10b) not only is analytic (and does not contain numerical integrations), but, most important, the summation over $\vec{\tau}_n$ is independent of the energy E and must be performed only once at the given wave vector of interest in the Brillouin zone. In Eq. (10b) the dependence on energy is indeed confined in the powers $(E+E_0)^I$ up to $I=I_0-1$ [apart from the factor $(\sqrt{E})^{-L}$]. With respect to Eq. (7b'), our Eq. (10b) exhibits the important advantages that the sum over index I is finite, and the computation of the Hankel functions is trivial (see the Appendix); in contrast, the unavoidable truncation of continued-fraction expansion needed in Eq. (7b') is indeed a delicate point.[13]

For the sake of completeness we give also the results in the case of a composite lattice with basis vectors $\vec{b}_1, \vec{b}_2, \ldots, \vec{b}_\nu$, again referring the reader to the Appendix for detailed proofs.

The expressions of the off-diagonal reduced structure constants $D_{LM}^{\mu\nu}(E,\vec{k})$ $(\mu\neq\nu)$ can be written in the form

$$D_{LM}^{\mu\nu}(E,\vec{k})=D_{LM}^{(1)\mu\nu}(E,\vec{k})+D_{LM}^{(2)\mu\nu}(E,\vec{k}) , \quad (11)$$

where

$$D_{LM}^{(1)\mu\nu}(E,\vec{k})=\frac{4\pi}{\Omega}\frac{(E+E_0)^{I_0}}{(\sqrt{E})^L}\sum_{\vec{k}_n}\frac{k_n^L e^{i\vec{k}_n\cdot(\vec{b}_\mu-\vec{b}_\nu)}}{(E-k_n^2)(E_0+k_n^2)^{I_0}}Y_{LM}(\vec{k}_n) , \quad (12a)$$

$$D_{LM}^{(2)\mu\nu}(E,\vec{k})=\frac{1}{(\sqrt{E})^L}\sum_{I=0}^{I_0-1}\frac{(-i)^I}{I!2^I}(E+E_0)^I\sum_{\vec{\tau}_n}|\vec{\tau}_n-\vec{b}_\mu+\vec{b}_\nu|^I e^{i\vec{k}\cdot\vec{\tau}_n}Y_{LM}(\vec{\tau}_n-\vec{b}_\mu+\vec{b}_\nu)$$

$$\times(\sqrt{E_0})^{L-I+1}h_{L-I}(i\sqrt{E_0}\,|\vec{\tau}_n-\vec{b}_\mu+\vec{b}_\nu|) . \quad (12b)$$

Note that for $\mu\neq\nu$ the term $D_{00}^{(3)}$ is no longer present; a phase factor appears in $D^{(1)}$, and the sum over $\vec{\tau}_n$ in $D^{(2)}$ includes $\vec{\tau}_n=0$.

Before closing this section, we wish to clarify further the *basic physical concept,* which is at the heart of our procedure for Eqs. (9)–(12). Disregarding factors unessential for the present reasoning, we consider sums of the type

$$S_1(E,\vec{k})=\sum_{\vec{k}_n}\frac{1}{E-k_n^2} ,$$

$$S_2(E,\vec{k})=\sum_{\vec{k}_n}\frac{1}{E-k_n^2}\frac{(E_0+E)^{I_0}}{(E_0+k_n^2)^{I_0}} ,$$

and we notice that S_1 and S_2 have the *same poles with the same residuals* (if $E_0>0$). Thus the difference S_1-S_2 is a well-behaved function, easy to evaluate by a series development. The sum S_2 is rapidly convergent when I_0 is sufficiently large, because the terms to be summed vary as $k_n^{-2-2I_0}$ for large k_n. Thus a convenient manner to evaluate S_1 is to compute S_2 and S_1-S_2. This is basically what our procedure[17] does through Eqs. (9)–(12).

D. Comparison with the Segall-Yang approach

It is interesting to compare our results with those of Segall and Yang.[4] The Segall-Yang approach makes great strides toward a drastic reduction of the employment of the Ewald algorithm but still requires its usage. On the other hand, our procedure fulfills this aim. Thus it is worthwhile to compare more closely the two procedures and clarify how our approach can be seen as a generalization of the Segall-Yang approach.

Consider expression (4) for the structure constants $D_{LM}(E,\vec{k})$ when $L\neq0$ (the case $L=0$ can be dealt with along similar lines). Following Ref. 4, we split the sum over the vectors k_n into two parts: one inside a sphere of (arbitrary) radius k_c and one outside it. We have

$$D_{LM}(E,\vec{k})=\frac{4\pi}{\Omega(\sqrt{E})^L}\left[\sum_{k_n<k_c}\frac{k_n^L}{E-k_n^2}Y_{LM}(\vec{k}_n)+\sum_{k_n\geq k_c}\frac{k_n^L}{E-k_n^2}Y_{LM}(\vec{k}_n)\right] . \quad (13)$$

For the $E<k_c^2$, with a series development of the denominators in the second sum of Eq. (13), we obtain

$$\frac{\Omega(\sqrt{E})^L}{4\pi}D_{LM}(E,\vec{k})=\sum_{k_n<k_c}\frac{k_n^L}{E-k_n^2}Y_{LM}(\vec{k}_n)-\sum_{k_n\geq k_c}Y_{LM}(\vec{k}_n)k_n^{L-2}\left[1+\frac{E}{k_n^2}+\cdots+\frac{E^i}{k_n^{2i}}+\cdots\right]$$

$$=\sum_{k_n<k_c}\frac{k_n^L}{E-k_n^2}Y_{LM}(\vec{k}_n)-\sum_{k_n\geq k_c}k_n^{L-2}Y_{LM}(\vec{k}_n)\left[\sum_{i=0}^{j-1}\frac{E^i}{k_n^{2i}}+O\left[\left[\frac{E}{k_c^2}\right]^j\right]\right], \quad (14)$$

where the order of magnitude of the residual terms is $(E/k_c^2)^j$.

It is convenient to define the quantities

$$f_{LM}^{(i)}(\vec{k})=-\sum_{k_n\geq k_c}k_n^{L-(2+2i)}Y_{LM}(\vec{k}_n)\,, \quad (15)$$

which can be evaluated with appropriate manipulations[4] of the Ewald sums. In terms of these auxiliary parameters, Eq. (14) can be written in the more compact form

$$\frac{\Omega(\sqrt{E})^L}{4\pi}D_{LM}(E,\vec{k})=\sum_{k_n<k_c}\frac{k_n^L}{E-k_n^2}Y_{LM}(\vec{k}_n)+\sum_{i=0}^{j-1}f_{LM}^{(i)}(\vec{k})E^i+O\left[\left[\frac{E}{k_c^2}\right]^j\right]. \quad (16)$$

Thus we recover the results of Segall and Yang, but our procedure allows an estimation of the accuracy of Eq. (16) and provides a criterion to improve it.

To make fully transparent the comparison of our procedure in Sec. II C, we define the quantities

$$g_{LM}^{(i)}(\vec{k})=-\sum_{\vec{k}_n}k_n^{L-(2+2i)}Y_{LM}(\vec{k}_n) \quad (17)$$

and exploit the identity

$$\frac{k_n^L}{E-k_n^2}+\frac{k_n^L}{k_n^2}\left[1+\frac{E}{k_n^2}+\cdots+\frac{E^{j-1}}{k_n^{2(j-1)}}\right]\equiv\frac{k_n^LE^j}{(E-k_n^2)k_n^{2j}}\,. \quad (18)$$

With the help of Eqs. (17) and (18), we transform Eq. (16) in the form

$$\frac{\Omega(\sqrt{E})^L}{4\pi}D_{LM}(E,\vec{k})=\sum_{k_n<k_c}\frac{k_n^LE^j}{(E-k_n^2)k_n^{2j}}Y_{LM}(\vec{k}_n)+\sum_{i=0}^{j-1}g_{LM}^{(i)}(\vec{k})E^i+O\left[\left[\frac{E}{k_c^2}\right]^j\right].$$

We now dispose of the residual terms of the order of $(E/k_c^2)^j$, letting $k_c\to\infty$. We have

$$\frac{\Omega(\sqrt{E})^L}{4\pi}D_{LM}(E,\vec{k})=\sum_{\vec{k}_n}\frac{k_n^LE^j}{(E-k_n^2)k_n^{2j}}Y_{LM}(\vec{k}_n)+\sum_{i=0}^{j-1}g_{LM}^{(i)}(\vec{k})E^i\,. \quad (19)$$

Equation (19), which summarizes the results of Segall and Yang, becomes equivalent to our equations (10) if in Eq. (14) the series development around $E=0$ of the term $(E-k_n^2)^{-1}$ is replaced by the series development around $E=-E_0$.

III. NUMERICAL APPLICATION: ENERGY BANDS OF SOLID NEON

In this section we briefly consider the specific case of the conduction bands of solid neon. The great amount of literature on this material (see, for instance, Refs. 18–22, and references quoted therein) allows checks of our procedure from a numerical point of view and comparison with different methods.

Solid neon crystalizes in the fcc structure; the lattice parameter a_0 has been taken equal to 8.43 a.u. as in Ref. 21. In our KKR application we wish to describe the s, p, and d character of the conduction bands; thus we are interested in the reduced structure coefficients with L up to 4. The structure coefficients $D_{LM}(E,\vec{k})$ are computed using Eq. (10) and Eq. (A16). The choice of the partition parameter E_0 and iteration number I_0 has been done in such a way as to produce a reasonable balance in the sums over reciprocal- and translational-lattice vectors. After some attempts and checks, the choice of the partition parameter of the order of 1 and of I_0 in the form $I_0=[L/2]+5$ was found to be quite satisfactory in the energy range (up to $\simeq$3 Ry) of our interest. The sums over reciprocal- and translational-lattice vectors could be safely terminated upon including about 50 terms in the former and about 100 terms in the latter. A somewhat higher number of terms in the direct-lattice sum is acceptable, since the direct-lattice sums in Eq. (10b) do not depend on energy and must be performed only once for a given $\vec{k}$ vector.

After computing the reduced structure coefficients up to $L=4$, the structure coefficients $\Gamma_{lm,l'm'}(E,\vec{k})$ with l,l' up to 2 are constructed in the standard way, and the KKR secular equation

$$||\Gamma_{lm,l'm'}(E,\vec{k})+\sqrt{E}\ \mathrm{cotg}\ \delta_l(E)\delta_{ll'}\delta_{mm'}||=0 \tag{20}$$

is then set up.

In the KKR equation (20) we have inserted the phase shifts calculated theoretically[23] for the isolated neon atom in the Hartree-Fock (HF) approximation. The assumption that the crystal potential is the sum of atomic nonoverlapping HF potentials appears reasonable[21] in view of the relatively large interatomic separation in the solid and of the closed-shell nature of the composing units.

The results are given in Table I, where we have also reported for sake of completeness the HF (at least in principle) calculations available in the literature with different methods. The practical coincidence between the present KKR calculation and the augmented-plane-wave (APW) results[21] when using the same phase shifts is evident.

A rather interesting point concerns the problem of correlation-polarization effects[19,25,26] on the band structure of large gap insulators. In order to estimate these effects on the conduction bands of neon, we have inserted in the KKR equation (20) the phase shifts obtained from electron-atom scattering experiments.[24] This procedure is justified if the crystal potential can be taken as the sum of nonoverlapping potentials, described by the experimental atomic phase shifts.

The correlated energy levels obtained in this way are reported in Table I. It can be noticed that the correlated energy bands shift almost rigidly $\simeq 1$ eV with respect to the HF energy bands, in the sense of a reduction of the energy gap. It is worthwhile to note that our KKR calculations confirm the usefulness of the semiempirical shift expression $\Delta E=\frac{1}{2}(e^2/R_{\mathrm{ML}})(1-1/\epsilon_s)\simeq 0.7$ eV, where $R_{\mathrm{ML}}=\pi a_0/6.3346=4.18$ a.u. is the Mott-Littleton radius of solid neon and $\epsilon_s=1.24$ is the static dielectric constant.

Finally, we notice from Table I that the bottom conduction state Γ_1^+ has positive energy ($+1.27$ eV) even if correlation effects are included. A negative electron affinity in solid neon is indeed necessary to explain the dynamics of atomic self-trapped excitons, recently investigated by transient absorption spectroscopy.[27]

IV. CONCLUSIONS

In this paper we have examined the problem of the calculation of the reduced structure constants in

TABLE I. Hartree-Fock conduction-band energies (eV) of neon at some symmetry points by different authors. The conduction-band energies corresponding to the experimental phase shifts are also reported. GOPW denotes Gaussian orthogonal-plane-wave method; APW denotes augmented-plane-wave method.

	Present work Phase shifts		Baroni *et al.*	Natalizi and Resta	Euwema *et al.*	Kunz and Mickish	Dagens and Perrot
	Expt. from Ref. 24	Theor. from Ref. 23	GOPW (Ref. 22)	APW (Ref. 21)	Gaussian local basis (Ref. 20)	Slater local basis (Ref. 19)	APW (Ref. 18)
Γ_1^+	1.27	2.51	1.99	2.51	2.85	2.21	2.67
Γ_5^+	20.34	21.15	22.08	21.16	29.25		20.81
X_1^+	8.34	9.20	9.42	9.22	13.58	15.5	9.19
X_2^-	9.44	10.46	7.69	10.46	10.42	10.4	10.18
X_4^+	13.15	14.00	14.74	14.00			13.89
X_5^-	17.66	18.37	15.88	18.38	18.28	19.8	17.84
L_2^-	7.15	8.16	5.69	8.15	8.38	8.10	7.92
L_1^+	7.68	8.77	8.52	8.77	9.52	9.99	8.75
L_3^+	18.80	19.53	20.31	19.53			19.21

the Green's-function method. We have provided a new algorithm, which turns out to be convenient and manageable. The new procedure, applicable also to composite lattices, is of value not only in the field of bulk electronic state calculations but also in other areas of research for which the Green's-function method is an invaluable tool.

APPENDIX

1. Some mathematical properties and identities

We recall the two representations of the structure constants $D_{LM}(E,\vec{k})$ in the extreme limits of summation either in direct or reciprocal space. From Eqs. (4) and (5) we have

$$D_{LM}(E,\vec{k})=\frac{4\pi}{\Omega}\frac{1}{(\sqrt{E})^L}\sum_{\vec{k}_n}\frac{k_n^L}{E-k_n^2}Y_{LM}(\vec{k}_n)+\frac{1}{\sqrt{4\pi}}\delta_{L0}\lim_{r\to 0}\frac{1}{r} \tag{A1}$$

and

$$D_{LM}(E,\vec{k})=-i^{1-L}\sqrt{E}\sum_{\vec{\tau}_n\neq 0}e^{i\vec{k}\cdot\vec{\tau}_n}h_L(\sqrt{E}\tau_n)Y_{LM}(\vec{\tau}_n)-\frac{i}{\sqrt{4\pi}}\sqrt{E}\,\delta_{L0}\,, \tag{A2}$$

where

$$h_L(x)\equiv h_L^{(1)}(x)=j_L(x)+in_L(x)\,.$$

If we compare the two expressions (A1) and (A2), we obtain an identity that is valid for any value of the energy E (positive or negative). We write down this identity for $E=-E_0$ (with $E_0>0$):

$$-\frac{4\pi}{\Omega}\sum_{\vec{k}_n}\frac{k_n^L}{E_0+k_n^2}Y_{LM}(\vec{k}_n)\equiv(\sqrt{E_0})^{L+1}\sum_{\vec{\tau}_n\neq 0}e^{i\vec{k}\cdot\vec{\tau}_n}h_L(i\sqrt{E_0}\tau_n)Y_{LM}(\vec{\tau}_n)+\frac{1}{\sqrt{4\pi}}\sqrt{E_0}\delta_{L0}-\frac{1}{\sqrt{4\pi}}\delta_{L0}\lim_{r\to 0}\frac{1}{r}\,. \tag{A3}$$

In the following we need an explicit expression of the derivative of order I with respect to E_0 of both members in Eq. (A3). To begin, consider the case of first-order derivative. We have

$$\frac{d}{dE_0}[(\sqrt{E_0})^{L+1}h_L(i\sqrt{E_0}\tau_n)]=\tfrac{1}{2}(\sqrt{E_0})^{L-1}[(L+1)h_L(i\sqrt{E_0}\tau_n)+i\sqrt{E_0}\tau_n h_L'(i\sqrt{E_0}\tau_n)]\,, \tag{A4}$$

where

$$h_L'(i\sqrt{E_0}\tau_n)=\left[\frac{d}{dx}h_L(x)\right]_{x=i\sqrt{E_0}\tau_n}\,.$$

We take advantage of the recurrence relations[16] for $h_L(x)$, which are valid for any integer L (positive, negative, or zero):

$$(L+1)h_L(x)+xh_L'(x)=xh_{L-1}(x)\,, \tag{A5}$$

$$\frac{2L+1}{x}h_L(x)=h_{L-1}(x)+h_{L+1}(x)\,. \tag{A6}$$

Exploiting the first of these two relations, we obtain for (A4)

$$\frac{d}{dE_0}[(\sqrt{E_0})^{L+1}h_L(i\sqrt{E_0}\tau_n)]=\frac{i\tau_n}{2}(\sqrt{E_0})^{L}h_{L-1}(i\sqrt{E_0}\tau_n)\,. \tag{A7}$$

Iterating Eq. (A7) I times, we obtain

$$\frac{d^I}{dE_0^I}[(\sqrt{E_0})^{L+1}h_L(i\sqrt{E_0}\tau_n)]=\left[\frac{i\tau_n}{2}\right]^I(\sqrt{E_0})^{L-I+1}h_{L-I}(i\sqrt{E_0}\tau_n)\,. \tag{A8}$$

With Eq. (A8) we can now perform the derivative of order I with respect to E_0 of both members in Eq. (A3). We obtain the important identity

$$-\frac{4\pi}{\Omega}\frac{d^I}{dE_0^I}\sum_{\vec{k}_n}\frac{k_n^L}{E_0+k_n^2}Y_{LM}(\vec{k}_n)\equiv\left[\frac{i}{2\sqrt{E_0}}\right]^I(\sqrt{E_0})^{L+1}\sum_{\vec{\tau}_n\neq 0}\tau_n^I e^{i\vec{k}\cdot\vec{\tau}_n}Y_{LM}(\vec{\tau}_n)h_{L-I}(i\sqrt{E_0}\tau_n)+\frac{2}{3}\frac{1}{\sqrt{4\pi}}\frac{3}{2}\frac{1}{2}\left[-\frac{1}{2}\right]\cdots\left[\frac{1}{2}-I+1\right]E_0^{1/2-I}\delta_{L0}-\frac{1}{\sqrt{4\pi}}\delta_{L0}\delta_{I0}\lim_{r\to 0}\frac{1}{r}\,. \tag{A9}$$

2. Case of one atom per unit cell

Consider the identity expressed by Eq. (8) of the main text. The same identity when iterated I_0 times gives

$$\frac{1}{k_n^2-E}\equiv\sum_{I=0}^{I_0-1}\frac{(E+E_0)^I}{(k_n^2+E_0)^{I+1}}+\frac{(E+E_0)^{I_0}}{(k_n^2-E)(k_n^2+E_0)^{I_0}}\ .$$

This last equation can be rewritten in the form

$$\frac{1}{k_n^2-E}=\sum_{I=0}^{I_0-1}\frac{(-1)^I}{I!}(E+E_0)^I\frac{d^I}{dE_0^I}\frac{1}{k_n^2+E_0}+\frac{(E+E_0)^{I_0}}{(k_n^2-E)(k_n^2+E_0)^{I_0}}\ . \tag{A10}$$

Expression (A10) can also be obtained by a Taylor expansion up to the order of I_0-1 of the term $(k_n^2-E)^{-1}$ around $E=-E_0$; the residual term is expressed exactly by the last term of (A10).

Substituting (A10) into (A1) we obtain

$$D_{LM}(E,\vec{k})=-\frac{4\pi}{\Omega}\frac{1}{(\sqrt{E})^L}\sum_{I=0}^{I_0-1}\frac{(-1)^I}{I!}(E+E_0)^I\frac{d^I}{dE_0^I}\sum_{\vec{k}_n}\frac{k_n^L}{k_n^2+E_0}Y_{LM}(\vec{k}_n)$$

$$+\frac{4\pi}{\Omega}\frac{(E+E_0)^{I_0}}{(\sqrt{E})^L}\sum_{\vec{k}_n}\frac{k_n^L}{(E-k_n^2)(E_0+k_n^2)^{I_0}}Y_{LM}(\vec{k}_n)+\frac{1}{\sqrt{4\pi}}\delta_{L0}\lim_{r\to 0}\frac{1}{r}\ . \tag{A11}$$

By inserting (A9) into (A11) we prove Eqs. (10) of the main text.

3. Some manipulations for computer programs

Although expressions (10) of the main text are simple, it is convenient to introduce some minor manipulations for computer programs. In particular, we can always express $D_{LM}(E,\vec{k})$ in real form, in the case of simple lattices.

It is convenient to define auxiliary functions $p_L(x)$ associated with the Hankel functions $h_L(x)$ by the relation

$$p_L(x)=-i^L h_L(ix)e^x\ . \tag{A12}$$

Using (A6), we find that the auxiliary functions $p_L(x)$ satisfy the recurrence relations

$$p_{L-2}(x)=p_L(x)-\frac{2L-1}{x}p_{L-1}(x)\ . \tag{A13}$$

In particular, we have

$$p_L(x)=p_{-L-1}(x)\ ,$$

$$p_0(x)=p_{-1}(x)=\frac{1}{x}\ , \tag{A14}$$

$$p_1(x)=p_{-2}(x)=\frac{1}{x}+\frac{1}{x^2}\ ,$$

etc. The auxiliary functions $p_L(x)$ are simple combinations of powers of $1/x$, very easy to construct.

We can write $D_{LM}^{(2)}(E,\vec{k})$, defined by Eq. (10b) of the main text, in the following form:

$$D_{LM}^{(2)}(E,\vec{k})=-\frac{(\sqrt{E_0})^{L+1}}{(\sqrt{E})^L}\sum_{I=0}^{I_0-1}\frac{(E+E_0)^I}{I!(2\sqrt{E_0})^I}\sum_{\vec{\tau}_n\neq 0}\tau_n^I p_{L-I}(\sqrt{E_0}\tau_n)e^{-\sqrt{E_0}\tau_n}e^{i\vec{k}\cdot\vec{\tau}_n}i^{-L}Y_{LM}(\vec{\tau}_n)\ . \tag{A15}$$

We can further simplify this expression using the following considerations:

(a) For any translation vector $\vec{\tau}_n$ there is also $-\vec{\tau}_n$.
(b) The spherical harmonics $Y_{LM}(\vec{\tau}_n)$ have parity $(-1)^L$ with respect to the inversion symmetry operation.
(c) $\exp(i\vec{k}\cdot\vec{\tau}_n)=\cos\vec{k}\cdot\vec{\tau}_n+i\sin\vec{k}\cdot\vec{\tau}_n$ can be split in even and odd parts with respect to inversion.
(d) All the other terms of (A15) depend on $\vec{\tau}_n$ only through the modulus τ_n.

The final expression of $D_{LM}^{(2)}(E,k)$, most convenient for computational purposes, can be written in the form

$$D^{(2)}_{LM}(E,\vec{k})=-(-1)^{[L/2]}\frac{(\sqrt{E_0})^{L+1}}{(\sqrt{E})^{L}}\sum_{I=0}^{I_0-1}\frac{(E+E_0)^I}{I!(2\sqrt{E_0})^I}$$

$$\times\sum_{\tau_n\neq 0}\tau_n^I p_{L-I}(\sqrt{E_0}\tau_n)e^{-\sqrt{E_0}\tau_n}Y_{LM}(\vec{\tau}_n)\times\begin{cases}\cos\vec{k}\cdot\vec{\tau}_n & \text{if } L\text{is even}\\ \sin\vec{k}\cdot\vec{\tau}_n & \text{if } L\text{is odd}\end{cases} \tag{A16}$$

where the symbol $[L/2]$ denotes the integer part of $L/2$.

4. Generalization to the case of a composite lattice

Consider now the case of a composite lattice with translation vectors $\vec{\tau}_n$ and basis vectors $\vec{b}_1,\vec{b}_2,\ldots,\vec{b}_\nu$. Besides the "diagonal" reduced structure constants $D^{\mu\nu}_{LM}(E,k)$ with $\mu=\nu$, which have been already discussed, we must consider the "off-diagonal" reduced structure constants $D^{\mu\nu}_{LM}(E,\vec{k})$ with $\mu\neq\nu$, which refer to one atom centered at $\vec{b}_\mu$ and the other at $\vec{b}_\nu$.

The expression for the "off-diagonal" reduced structure constants in direct or reciprocal space presents only some formal differences with respect to (A1) and (A2). We have, in fact,

$$D^{\mu\nu}_{LM}(E,\vec{k})=\frac{4\pi}{\Omega}\frac{1}{(\sqrt{E})^L}\times\sum_{\vec{k}_n}\frac{k_n^L e^{i\vec{k}_n\cdot(\vec{b}_\mu-\vec{b}_\nu)}}{E-k_n^2}Y_{LM}(\vec{k}_n),\quad \mu\neq\nu\,. \tag{A17}$$

With respect to (A1) the absence of the singular term and the presence of appropriate phase factors can be noted.

The sum over the direct lattice is

$$D^{\mu\nu}_{LM}(E,\vec{k})=-i^{1-L}\sqrt{E}\times\sum_{\vec{\tau}_n}e^{i\vec{k}\cdot\vec{\tau}_n}h_L(\sqrt{E}\mid\vec{\tau}_n-\vec{b}_\mu+\vec{b}_\nu\mid)\times Y_{LM}(\vec{\tau}_n-\vec{b}_\mu+\vec{b}_\nu)\,,\quad \mu\neq\nu\,. \tag{A18}$$

Again, we have minor formal differences with respect to (A2).

We can now repeat step by step, starting from (A17) and (A18), the considerations that were given beginning at (A1) and (A2), and we prove in this way the equations (12) of the main text.

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