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ARTICLES

Ab initio Hartree-Fock computation of the electronic static structure factor for crystalline insulators: Benchmark results on LiF

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In this paper, we present a fully *ab initio* Hartree-Fock approach aimed at calculating the static structure factor of crystalline insulators at arbitrary values of momentum transfer. In particular, we outline the computation of the incoherent scattering function, the component of the structure factor that governs the incoherent x-ray scattering from solids. The presented theory is applied to crystalline LiF to obtain benchmark Hartree-Fock values for its incoherent scattering function. Benchmark theoretical values such as this, can be combined with the experimentally measured static structure factor, to understand the influence of electron correlation effects on cohesive properties of solids. [S0163-1829(99)11231-1]

I. INTRODUCTION

In order to obtain an *ab initio* understanding of the electronic structure of solids, it is essential to understand the nature of electron correlations in them.[1] Correlation being a real-space phenomenon, one possible way of visualizing it is through the density-density correlation function defined as

$$S(\mathbf{r}',\mathbf{r})=\frac{1}{N_0}\langle\Phi|\hat{\rho}(\mathbf{r}')\hat{\rho}(\mathbf{r})|\Phi\rangle, \tag{1}$$

where $|\Phi\rangle$ denotes the many-particle wave function of the system, N_0 is the total number of electrons in the system and $\hat{\rho}(\mathbf{r})=\Sigma_{i=1}^{N_0}\delta(\mathbf{r}-\mathbf{r}_i)$ is the density operator with $\mathbf{r}_i$ being the coordinates of the ith electron. One can easily show

$$S(\mathbf{r}',\mathbf{r})=\delta(\mathbf{r}'-\mathbf{r})+(N_0-1)g(\mathbf{r}',\mathbf{r}), \tag{2}$$

where $g(\mathbf{r}',\mathbf{r})$ is the electron pair-correlation function defined as

$$g(\mathbf{r}',\mathbf{r})=\frac{1}{\rho(\mathbf{r})\rho(\mathbf{r}')}\left\langle\Phi\left|\sum_{i\neq j}\delta(\mathbf{r}'-\mathbf{r}_i)\delta(\mathbf{r}-\mathbf{r}_j)\right|\Phi\right\rangle. \tag{3}$$

Above, $\rho(\mathbf{r})$ denotes the electronic charge density. Pair-correlation function represents the probability that when one electron is observed say at point $\mathbf{r}'$, another electron will be found in a characteristic volume $1/(N_0-1)$ located at $\mathbf{r}$.[1] Clearly, it can be used to quantify the so-called ''exchange-correlation hole'' associated with an electron in a many-electron system.[1] If we compute the Fourier transform of the density-density correlator, we obtain the static structure factor $S(\mathbf{Q})$ defined by

$$S(\mathbf{Q})=\frac{1}{N_0}\int d\mathbf{r}d\mathbf{r}'e^{i\mathbf{Q}\cdot(\mathbf{r}-\mathbf{r}')}S(\mathbf{r}',\mathbf{r})$$
$$=\frac{1}{N_0}\left\langle\Phi\left|\sum_{j,k}e^{i\mathbf{Q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}\right|\Phi\right\rangle. \tag{4}$$

If we assume that the system under consideration is a crystalline system with N unit cells, each of which has Z electrons in it so that $N_0=NZ$, we can decompose $S(\mathbf{Q})$ as a sum of a ''coherent'' and an ''incoherent'' part

$$S(\mathbf{Q})=\frac{N}{Z}\delta_{\mathbf{Q},\mathbf{G}}|F(\mathbf{Q})|^2+S_{inc}(\mathbf{Q}), \tag{5}$$

where $\mathbf{G}$ is a vector of the reciprocal lattice and the form factor $F(\mathbf{Q})$ defined as

$$F(\mathbf{Q})=\sum_{j=1}^{N_0}\langle\Phi|e^{i\mathbf{Q}\cdot\mathbf{r}_j}|\Phi\rangle, \tag{6}$$

can be easily seen to be the Fourier transform of the charge density of the system, while

$$S_{inc}(\mathbf{Q})=\frac{1}{NZ}\left(\sum_{j,k=1}^{N_0}\langle\Phi|e^{i\mathbf{Q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}|\Phi\rangle-|F(\mathbf{Q})|^2\right) \tag{7}$$

is referred to as the incoherent scattering function in the literature. It is intuitively obvious that being the expectation value of a two-electron operator, $S_{inc}(\mathbf{Q})$ will be sensitive to electron correlations in the crystal, while $F(\mathbf{Q})$, which is a one-electron operator, should be relatively insensitive to such effects. It is easy to verify that $S_{inc}(\mathbf{Q})$ satisfies limiting conditions

$$\lim_{Q\to 0}S_{inc}(\mathbf{Q})=0, \tag{8}$$

and

$$\lim_{Q\to\infty}S_{inc}(\mathbf{Q})=1. \tag{9}$$

One can perform the measurement of the static structure factor of a many-electron system in a variety of experiments such as electron scattering and x-ray scattering. For isolated atoms and molecules both electrons[2] and x-rays[3] are frequently used for such measurements, however, for crystalline systems, x-ray scattering appears to be the method of choice.[4–8] In such measurements, the quantity **Q** in equations above is identified with the momentum transferred by the incident particle (electron or photon), to the many-electron system under investigation. Keeping in mind the relationship between the static structure factor and the pair-correlation function [cf. Eqs. (2) and (4)], it is thus possible to obtain the pair-correlation function from these measurements. However, in what follows, we will devote exclusively on the x-ray scattering-based experiments. The coherent x-ray scattering (Bragg scattering), i.e., when the momentum transfer **Q** is equal to one of the vectors **G** of the reciprocal lattice, is governed predominantly by the form factor $F(\mathbf{Q})$. However, by concentrating on the measurements corresponding to those values of momentum transfer that are not equal to any reciprocal lattice vector, one can—according to Eq. (5)—directly measure the incoherent scattering function. The experiments that concentrate on this region of **Q** correspond to incoherent x-ray scattering. For the case of incoherent scattering of x-rays from a crystalline solid at finite temperatures, assuming that the energy of the incoming x-rays is much higher compared to the binding energies of the constituent electrons, but still low compared to the rest energy of the electron m_0c^2 (so that the relativistic effects can be neglected), the scattering cross section, for a solid composed of light elements, can be approximated as[5–7]

$$\frac{d\sigma}{d\Omega}\simeq r_0^2 N\left[\left(\frac{k}{k_0}\right)^2(\tilde{e}_0\cdot\tilde{e})^2 S_{inc}(\mathbf{Q})+S_{TDS}(\mathbf{Q})\right], \qquad (10)$$

where r_0 is the classical electron radius, $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of incoming and outgoing photons, $\tilde{e}_0$ and $\tilde{e}$ are the corresponding polarization vectors, $\mathbf{Q}=\mathbf{k}-\mathbf{k}_0$ is the momentum transfer while $S_{TDS}(\mathbf{Q})$ is the structure factor due to the thermal diffuse scattering caused both by the thermal, and the zero-point vibrations of the lattice. Thus, $S_{TDS}(\mathbf{Q})$ quantifies the contribution of phonons to the x-ray scattering, and can be computed by taking one-phonon, and higher order terms into account.[6,7] Therefore, by measuring the incoherent x-ray scattering cross section for different values of the momentum transfer **Q**, combined with the knowledge of $S_{TDS}(\mathbf{Q})$, one can, using Eq. (10), extract the incoherent scattering function $S_{inc}(\mathbf{Q})$ of the system under consideration.

Sacchetti and coworkers[5,8] have been the proponents of using the incoherent x-ray scattering to measure the static structure factor of crystalline compounds, for its subsequent use in the analysis of electron correlation effects. They have performed a series of accurate measurements of the static structure factor of the metallic system Be (Ref. 6) and the covalent system diamond[7] to obtain their pair-correlation functions, and analyzed various contributions to the ground-state energies of these compounds. In their latest experiment performed on crystalline LiF, they have, for the first time, subjected an ionic system to a similar analysis.[9] However, in order to quantify the contribution of electron correlation effects to the experimentally measured static structure factor in such experiments, benchmark Hartree-Fock (HF) results for the quantity are needed. It is the purpose of this paper to present a formalism using which one can perform such benchmark HF calculations within an *ab initio* framework. Indeed, Calzuola *et al.*,[9] by comparing their experimentally measured values of the static structure factor, to the benchmark HF values presented here, have estimated the correlation contribution to the cohesive energy of LiF. Therefore, the aim of these calculations is *not* to explain the experimental data, but rather to provide a theoretical reference, with respect to which the correlation effects can be quantified in the experimentally measured quantities. The formalism for computing the static structure factor presented here is based on a Wannier-function-based *ab initio* HF approach developed recently by us.[10,11] The approach has since been applied to compute the ground state properties of a number of ionic[12,13] and covalent compounds[14,15], including the form factor $[F(\mathbf{Q})]$ of LiF.[11]

The remainder of the paper is organized as follows. In Sec. II, we describe our formalism for the *ab initio* evaluation of the incoherent scattering function within an HF approach. An explicit formula is presented which represents $S_{inc}(\mathbf{Q})$ in terms of the Wannier functions of an infinite crystal. Our numerical results for LiF are presented in Sec. III, which are compared to the experimental results of Calzuola *et al.*[9] for the same compound. Finally, our conclusions are presented in Sec. IV.

II. THEORY

Here, we outline the evaluation of the incoherent scattering function $S_{inc}(\mathbf{Q})$ for an infinite crystalline insulator within an *ab initio* restricted Hartree-Fock (RHF) approach. Although, we are not aware of such a prior calculation for an infinite solid, we note that *ab initio* calculations are performed on a routine basis on isolated atoms[16–28] and molecules,[29–34] both at the HF, and the correlated level. However, for condensed-matter systems, perhaps because of practical difficulties associated with providing a wave-function-based *ab initio* description of an infinite system, such calculations are either performed assuming a jellium model for the electrons of the system,[4,6] or within the framework of the density-functional theory, which often involves phenomenological approximations.[35]

We assume that the compound under consideration is a closed-shell crystalline system whose RHF ground state can be described by n_c doubly occupied Wannier functions per unit cell, so that $Z=2n_c$. If we use Greek indices α, β etc. to denote the Wannier functions localized in a given unit cell, the RHF wave function of the infinite crystal can be described as a Slater determinant composed of the infinitely many Wannier functions $\{|\alpha(\mathbf{R}_j)\rangle;\alpha=1,n_c;j=1,N\}$, where $|\alpha(\mathbf{R}_j)\rangle$ denotes the αth Wannier function of a unit cell located at the position given by the vector $\mathbf{R}_j$ of the lattice. The aforementioned Wannier functions are assumed to form an orthonormal set

$$\langle\alpha(\mathbf{R}_i)|\beta(\mathbf{R}_j)\rangle=\delta_{\alpha\beta}\delta_{ij}, \qquad (11)$$

and Wannier functions localized in different unit cells are translated copies of each other

$$|\alpha(\mathbf{R}_i+\mathbf{R}_j)\rangle=\mathcal{T}(\mathbf{R}_i)|\alpha(\mathbf{R}_j)\rangle, \qquad (12)$$

where the operator $\mathcal{T}(\mathbf{R}_i)$ represents a translation by lattice vector $\mathbf{R}_i$. The theory and several applications of our approach, which directly obtains the RHF Wannier functions of a crystalline insulator (ionic or covalent), have been presented in several papers.[10–15]

If we use the standard formula for the expectation value of a two-particle operator with respect to a Slater determinant,[37] one can, after some algebraic manipulations, show that in the Wannier representation the RHF expression for the incoherent scattering function [cf. Eq. (7)] is given by

$$S_{inc}(\mathbf{Q}) = 1 - \frac{2}{Z} \sum_{\alpha,\beta=1}^{n_c} \sum_{i=1}^{N} |\langle \beta(\mathbf{R}_i) | e^{i\mathbf{Q}\cdot\mathbf{r}} | \alpha(\mathbf{0}) \rangle|^2, \quad (13)$$

where $|\alpha(\mathbf{0})\rangle$ represents a Wannier function localized in the reference unit cell. Equation (13) constitutes the key formula of this work, a detailed derivation of which is presented in the appendix. Since the Wannier functions in our computer code are represented in terms of Gaussian lobe-type localized basis functions, it is possible to write down analytic expressions for the matrix elements needed to evaluate $S_{inc}(\mathbf{Q})$ according to the expression above. The lattice sum over lattice vectors $\mathbf{R}_i$ involved in Eq. (13) decreases rapidly as one moves away from the reference cell, and is terminated once the convergence within a given threshold is achieved.

The restriction of the present approach to insulators stems from our use of Wannier functions as the single-particle orbitals, rather than the conventional Bloch orbitals. It is easy to see that the same theory can be easily extended to metallic systems if one were to express the many-body wave function of the solid in terms of Bloch orbitals. In that case, of course, the real-space sum [cf. Eq. (13)] will have to be replaced by an integration over the Brillouin zone. We will present this generalization in a future paper. This will be particularly useful in light of the future experiments which Sacchetti and coworkers are planning on metallic systems.[36]

III. RESULTS AND DISCUSSION

In this section, we present the results of our HF calculations of the incoherent scattering function at different values of the momentum transfer, and compare our results to the experimental ones. It is intuitively obvious, however, that HF structure factors can only describe the experimental results qualitatively—in order to obtain a better quantitative description theoretically, inclusion of electron correlation effects is essential. Nevertheless, in our opinion, the comparison with experiments is very instructive, because one can, in a rather pictorial way, see the successes and failures of the HF approximation in describing the physics of weakly-correlated systems.

The basis set used to represent the Wannier functions in our calculations was the lobe representation of the basis set proposed by Prencipe *et al.* in their Bloch-orbital-based HF study of the structural properties of LiF.[38] The basis set consisted of contracted Cartesian Gaussian-type basis functions and was of $[4s,3p]$ type for the fluorine atom, and $[2s,1p]$ for the lithium atom. For further details pertaining to the exponents and the contraction coefficients we refer to the original work.[38] Details dealing with the lobe representation of the Cartesian Gaussian basis functions can be found, e.g, in our previous paper.[11] We also examined the basis-set dependence of our results on $S_{inc}(\mathbf{Q})$ by performing calculations with larger basis sets that also included d-type basis functions on F atom, however, we did not observe any significant change in the results. Thus, we believe that our results on $S_{inc}(\mathbf{Q})$ presented below are fairly accurate.

TABLE I. Comparison of the Hartree-Fock incoherent scattering function $[ZS_{inc}(Q)]$ computed in this work with those measured in the experiment of Calzuola *et al.* (Ref. 9) at selected values of momentum transfer $\mathbf{Q}$. The momentum transfer was along the [100] direction in both the experiment and the theory.

Q	$ZS_{inc}(Q)$	
(a.u.)	This Work	Experiment
0.000	0.0000	
0.100	0.0337	
0.200	0.1352	
0.300	0.2993	
0.400	0.5188	
0.517	0.8346	0.4434
0.569	0.9919	0.6446
0.621	1.1579	0.8832
0.672	1.3279	1.0774
0.724	1.5075	1.3008
1.034	2.6569	2.4282
1.137	3.0499	2.7480
1.291	3.6321	3.2082
1.497	4.3856	3.7112
1.650	4.9182	4.3404
1.804	5.4265	4.7896
1.957	5.9019	5.3122
2.110	6.3461	5.8166
2.263	6.7583	6.3042
2.465	7.2525	6.6888
2.768	7.8896	7.3224
3.169	8.5596	7.9372
3.368	8.8304	8.5186
3.467	8.9521	8.3750
3.763	9.2716	9.2784
3.958	9.4506	9.6102
7.219	10.7878	10.9616
7.301	10.8060	10.9484
7.382	10.8237	10.9196
7.622	10.8747	10.8880
9.000	11.1331	
10.000	11.2894	
12.000	11.5336	
14.000	11.7009	
15.000	11.7618	

In the theoretical calculations the observed face-centered cubic (fcc) structure was assumed for the compound. The reference unit cell was taken to be the primitive cell with the F atom at (0,0,0) position and the Li atom at $(0,0,a/2)$, where a is the lattice constant. For the lattice constant, the room temperature value of 4.02 Å was used.

The results of our calculations are summarized in Table I and Fig. 1, which present $ZS_{inc}(\mathbf{Q})$ as a function of the momentum transfer $\mathbf{Q}$, where $Z=12$ for the case of LiF. Direction of the momentum transfer for both the theory and the experiment was along [100] direction. Theoretical HF

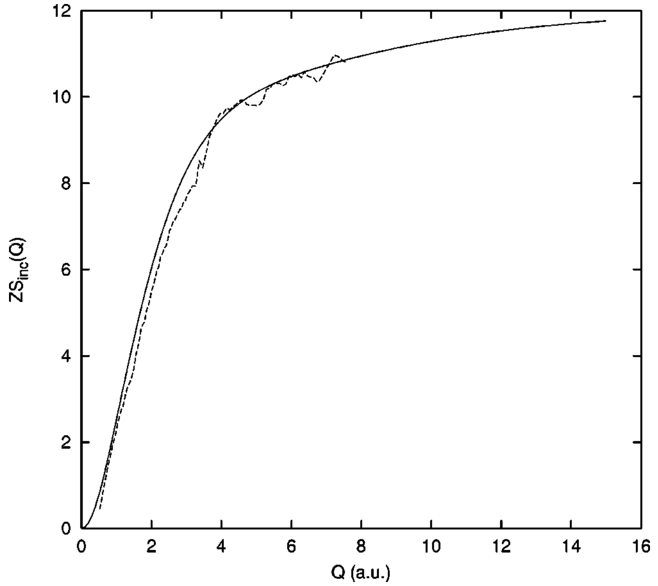

FIG. 1. $ZS_{inc}(Q)$ plotted as a function of the momentum transfer Q in the direction [100]. Solid line represents the HF theoretical results of this work, while the dashed line represents the experimental results of Calzuola *et al.* (Ref. 9). The experimental data was confined to the values of Q ranging from 0.517 a.u. to 7.622 a.u.

values of $S_{inc}(\mathbf{Q})$ were calculated with the magnitude of the momentum transfer Q ranging from 0.0 to 15.0 atomic units (a.u.). For the experimental data, Q ranged from 0.517 to 7.622 a.u. It is quite clear from Fig. 1 that HF theory is in good qualitative agreement with the experimental result, which is a manifestation of the fact that LiF is a weakly correlated system. In order to quantify the correlation effects, we define the quantity $E(\mathbf{Q}) = S_{inc}^{HF}(\mathbf{Q}) - S_{inc}^{exp}(\mathbf{Q})/S_{inc}^{exp}(\mathbf{Q}) \times 100$, which clearly measures the percentile contribution of electron correlation effects to the experimentally measured $S_{inc}(\mathbf{Q})$, using the HF values presented here as the benchmark reference. $E(\mathbf{Q})$ is plotted in Fig. 2, as a function of Q. For the smallest value of the momentum transferred measured $Q=0.517$ a.u., the correlation contribution is 88.2%. With the increasing momentum transfer the correlation contribution decreases rapidly staying in the range 10.0—20.0% from $Q=0.724$ to $Q=2.059$ a.u. From $Q=3.664$ a.u. onwards the upper bound for the correlation contribution is approximately three percent, while most of the points are in one to two percent range. We also see some oscillations in the $E(\mathbf{Q})$ as a function of the momentum transfer, which may be due to the experimental uncertainties. However, the general trend in $E(\mathbf{Q})$ as a function of the momentum transfer $\mathbf{Q}$ is clear—the contribution due to the correlation effects decreases with the increasing momentum transfer. This trend is also observed in the calculations involving free atoms and molecules where the HF calculations for small values of momentum transfer always overestimate $S_{inc}(\mathbf{Q})$ as compared to the correlated ones.[16–34] This trend can be understood as follows. HF theory, because of a lack of correlations in it, will always overestimate the pair-correlation function $g(\mathbf{r}',\mathbf{r})$ and consequently $S_{inc}(\mathbf{Q})$. Since for small values of momentum transfer Q, one can only probe the valence electrons, the main contribution to $S_{inc}(\mathbf{Q})$ will also naturally come from these electrons. However, it is the valence electrons for which the correlation effects are quantitatively the most important, and their neglect in the HF approach leads to relatively large deviations, as compared to the experimental values, for smaller values of momentum transfer.

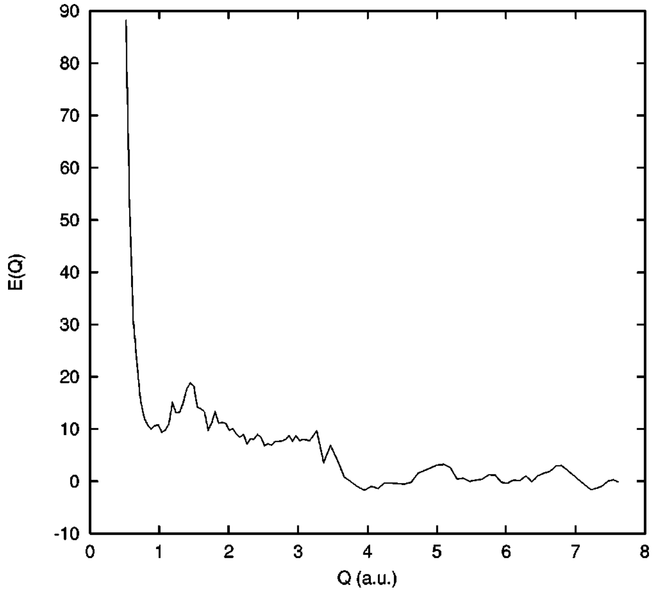

FIG. 2. Relative correlation contribution $E(Q)$ to the measured $S_{inc}(\mathbf{Q})$, plotted as a function of the momentum transfer Q. The momentum transfer direction was [100]. See text for details.

In our calculations we did not observe any significant anisotropy in $S_{inc}(\mathbf{Q})$ with respect to the direction of $\mathbf{Q}$. We performed the same set of calculations for $S_{inc}(\mathbf{Q})$ for momentum transfer directions [110] and [111] as well, however, the difference in the results compared to [100] direction was always less than 1.0×10^{-5}. This result can also be understood on intuitive grounds as the charge density in LiF is fairly isotropic, therefore, one would not expect the incoherent scattering function to show any anisotropy. Finally, it is clear from both Table I and Fig. 1 that our HF results on $S_{inc}(\mathbf{Q})$ approach the correct limiting values in both the low-momentum-transfer region [cf. Eq. (8)] and the high-momentum-transfer region [cf. Eq. (9)].

IV. CONCLUSIONS

In conclusion, a wave-function-based fully *ab initio* approach has been presented, using which, one can compute the static structure factor of a crystalline compound at arbitrary values of the momentum transfer, at the HF level. The formalism was applied to the case of crystalline LiF, and benchmark values were obtained for its incoherent scattering function. These values were used in the analysis of a recently performed incoherent x-ray scattering experiment on LiF to quantify the electron correlation effects, in general, and to predict the correlation contribution to its cohesive energy, in particular.[9] In case such experimental measurements are performed on other insulating compounds, one can use the formalism presented here to perform similar benchmark calculations on those systems as well. The present version of the theory is restricted to insulating systems because of its Wannier-function-based formulation, however, in light of the planned future experiments on metallic systems,[36] we do intend to develop an *ab initio* HF formalism meant for computing $S_{inc}(\mathbf{Q})$ for gapless systems, as well.

Although the aim of the present HF formalism was not to explain the experimental data, but rather to facilitate its analysis, it is still of interest to include electron correlation effects theoretically. Indeed, recently, we have generalized our Wannier-function-based approach to include electron correlation effects by systematically enlarging the many-particle ground-state wave function by considering virtual excitations from the space of the occupied Wannier functions to that of the virtual ones.[39] The approach was demonstrated by computing the correlation contributions to the total energy per unit cell of bulk LiH.[39] However, the generalization of the approach to compute the correlated expectation value of an operator other than the Hamiltonian is far from trivial, and will be the subject of a future investigation.

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APPENDIX

Our aim in the present section is to present a derivation of Eq. (13) of the text which is an RHF level expression for $S_{inc}(\mathbf{Q})$ in terms of corresponding Wannier functions. Equation (7) which defines $S_{inc}(\mathbf{Q})$ involves the expectation value of the operator

$$X(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_0};\mathbf{Q})=\sum_{j,k=1}^{N_0} e^{i\mathbf{Q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}. \tag{A1}$$

Although operator $X(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_0};\mathbf{Q})$ is a sum of two-electron terms, however, unlike other similar operators such as the Coulomb interaction operator, the sum in Eq. (A1) does contain the term where $j=k$. Therefore, in order to utilize the well-established formulas for matrix elements of two-electron operators between Slater determinant,[37] we rewrite Eq. (A1) as

$$\begin{aligned}X(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_0};\mathbf{Q})={}&N_0+Y(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_0};\mathbf{Q})\\&+Y^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_0};\mathbf{Q}),\end{aligned} \tag{A2}$$

where the first term on the right-hand side corresponds to $j=k$ terms of the sum in Eq. (A1) and the operator Y is defined as

$$Y(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_0};\mathbf{Q})=\sum_{j<k} e^{i\mathbf{Q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}. \tag{A3}$$

Y^*, which represents the complex conjugate of operator Y, can be easily deduced from Eq. (A3). It is clear that Y (and hence, Y^*) as defined above are traditional two-electron operators. Utilizing the well-known formula for the expectation value of a general two-electron operator $G=\Sigma_{j<k}g(\mathbf{r}_j,\mathbf{r}_k)$ with respect to a single Slater determinant state $|\Psi\rangle$ (Ref. 37)

$$\begin{aligned}\langle\Psi|G|\Psi\rangle={}&\frac{1}{2}\sum_{a,b}\langle ab|g(\mathbf{r}_1,\mathbf{r}_2)|ab\rangle\\&-\frac{1}{2}\sum_{a,b}\langle ba|g(\mathbf{r}_1,\mathbf{r}_2)|ab\rangle,\end{aligned} \tag{A4}$$

where $|a\rangle$, $|b\rangle$ are the orbitals constituting the Slater determinant, one can easily get

$$\begin{aligned}\langle\Phi|Y|\Phi\rangle={}&\sum_{\alpha,\beta=1}^{n_c}\sum_{\mathbf{R}_i,\mathbf{R}_j=1}^{N}\{2\langle\alpha(\mathbf{R}_i)|e^{i\mathbf{Q}\cdot\mathbf{r}}|\alpha(\mathbf{R}_i)\rangle\\&\times\langle\beta(\mathbf{R}_j)|e^{-i\mathbf{Q}\cdot\mathbf{r}}|\beta(\mathbf{R}_j)\rangle-\langle\beta(\mathbf{R}_j)|e^{i\mathbf{Q}\cdot\mathbf{r}}|\alpha(\mathbf{R}_i)\rangle\\&\times\langle\alpha(\mathbf{R}_i)|e^{-i\mathbf{Q}\cdot\mathbf{r}}|\beta(\mathbf{R}_j)\rangle\},\end{aligned} \tag{A5}$$

where $|\Phi\rangle$ represents the single-Slater-determinant RHF ground state of the crystalline insulator under consideration. As discussed in Sec. II, it is expressed in terms of Wannier functions $\{|\alpha(\mathbf{R}_j)\rangle;\alpha=1,n_c;j=1,N\}$, where $2n_c$ is the number of electrons per unit cell and N is the total number unit cells considered. In order to arrive at the right-hand side of Eq. (A5) spin summations have been performed, and the first term represents the so-called ''direct'' contribution, while the second term represents the ''exchange'' contribution. It is clear that both the direct, as well as the exchange terms are expressed as products of two one-electron matrix elements, which are complex conjugates of each other. Moreover, using the defining Eq. (6), one can easily see that, for the RHF state considered here, the direct term of Eq. (A5) is nothing but the product of the form factor $F(\mathbf{Q})$ and its complex conjugate, leading to

$$\begin{aligned}\langle\Phi|Y|\Phi\rangle={}&\frac{1}{2}F(\mathbf{Q})|^2\\&-\sum_{\alpha,\beta=1}^{n_c}\sum_{\mathbf{R}_i,\mathbf{R}_j=1}^{N}|\langle\beta(\mathbf{R}_j)|e^{i\mathbf{Q}\cdot\mathbf{r}}|\alpha(\mathbf{R}_i)\rangle|^2.\end{aligned} \tag{A6}$$

Finally, using the translational invariance property of the one-electron matrix elements $\langle\beta(\mathbf{R}_j)|e^{i\mathbf{Q}\cdot\mathbf{r}}|\alpha(\mathbf{R}_i)\rangle=\langle\beta(\mathbf{R}_j-\mathbf{R}_i)|e^{i\mathbf{Q}\cdot\mathbf{r}}|\alpha(\mathbf{0})\rangle$, and by rearranging the sum over lattice vectors $\mathbf{R}_i$ and $\mathbf{R}_j$ in Eq. (A6), one gets in the infinite solid limit ($N\to\infty$)

$$\langle\Phi|Y|\Phi\rangle=\frac{1}{2}|F(\mathbf{Q})|^2-N\sum_{\alpha,\beta=1}^{n_c}\sum_{\mathbf{R}_i=1}^{N}|\langle\beta(\mathbf{R}_i)|e^{i\mathbf{Q}\cdot\mathbf{r}}|\alpha(\mathbf{0})\rangle|^2. \tag{A7}$$

If we combine the results of Eqs. (A1), (A2), (A7), and substitute them in Eq. (7), we immediately obtain Eq. (13), valid for a single-Slater determinant RHF wave function $|\Phi\rangle$.

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[3] For a recent study of static structure factor and electron correlation effects in several organic molecules by means of inelastic x-ray scattering method see, e.g., N. Watanabe, H. Hayashi, Y. Udagawa, S. Ten-no, and S. Iwata, J. Chem. Phys. **108**, 4545 (1998).

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