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Dyson Orbitals, Quasi-Particle effects and Compton scattering

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Dyson orbitals play an important role in understanding quasi-particle effects in the correlated ground state of a many-particle system and are relevant for describing the Compton scattering cross section beyond the frameworks of the impulse approximation (IA) and the independent particle model (IPM). Here we discuss corrections to the Kohn-Sham energies due to quasi-particle effects in terms of Dyson orbitals and obtain a relatively simple local form of the exchange-correlation energy. Illustrative examples are presented to show the usefulness of our scheme.

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I. INTRODUCTION

Dyson orbitals are a set of one-particle orbitals that are associated with many-electron wavefunctions. These orbitals connect the exact ground-state of the N-electron system with excited states containing $N-1$ or $N+1$ electrons. The importance of Dyson orbitals in understanding Compton scattering spectra has been emphasized recently by Kaplan et *al.* [1], who present a general formalism for the Compton cross section, which goes beyond the standard treatment involving the frameworks of the impulse approximation (IA) and the independent particle model (IPM). The breakdown of the IA in describing core Compton profiles is well-known [2]. More recently, high resolution valence Compton profiles (CPs) of Li at relatively low photon energy of $8-9$ keV have been found to show asymmetries in shape and smearing of the Fermi surface (FS) features where deviations from the IA have been implicated [3, 4].

Dyson orbitals also give insight into quasi-particle effects in the correlated ground state of the many body system. In this article, we focus on understanding energies of one-particle excitations of the ground state, which play an important role not only in the formalism of the Compton scattering cross-section, but also in the band structure problem more generally. To this end, a Green's function approach is used to first obtain an expression for the exchange-correlation energy in terms of the self-energy operator involved in the description of the Dyson orbitals. A local ansatz for the self-energy is then invoked to obtain a relatively simple expression for the excitation energies. We illustrate our scheme by considering the example of first ionization energies of low Z atoms from $Z=1$ (H) to $Z=6$ (C) and find good agreement with the corresponding experimental results. As another example, the measured bandgap in diamond is also reproduced reasonably by our computations.

An outline of this article is as follows. The introductory remarks are followed in Section II by a brief overview of the general formalism of Ref. [1] for the Compton scattering cross section. The importance of properly including excitation energies in the computation for describing the asymmetry of the CP around $q=0$ is stressed. Section III presents the Green's function formulation and discusses our scheme for computing excitation energies. Section IV gives a few illustrative applications of the theory, followed in Section V by a few concluding remarks.

II. DYSON ORBITALS AND COMPTON SCATTERING

The Dyson spin-orbital g_n can be defined in terms of the many-body ground-state wavefunction Ψ_0 and the wavefunction Ψ_n of the singly ionized excited system characterized by the quantum number n [5, 6, 7, 8]:

$$g_n(\mathbf{x}_N) = \sqrt{N} \int \Psi_n(\mathbf{x}_1....\mathbf{x}_{N-1})^* \Psi_0(\mathbf{x}_1....\mathbf{x}_N)\, d\mathbf{x}_1....d\mathbf{x}_{N-1} \ , \tag{1}$$

where the index $\mathbf{x}$ denotes both spatial and spin coordinates and the integration over $d\mathbf{x}_i$ implicitly includes a summation over the spin coordinates. The Dyson orbitals thus give generalized overlap amplitudes between the ground state and the singly ionized states of the many body system. Note that, in general, Dyson orbitals do not form an orthonormal set. The Dyson spin-orbital with the spin projection σ may be written in terms of the spin function $\sigma(\zeta)$ as

$$g_n(\mathbf{x}) = g_n(\mathbf{r}, \sigma(\zeta)) = g_n(\mathbf{r})\sigma(\zeta) \ . \tag{2}$$

The excitation energy $E_b^{(n)}$ associated with the nth Dyson orbital is given by

$$E_b^{(n)} = E_n(N-1) - E_0(N) \tag{3}$$

where $E_0(N)$ is the N-particle ground state energy and $E_n(N-1)$ is the energy of the $(N-1)$ particle ionized system when it is in its nth quantum state. Eqs. 1-3 above define what may be thought of as occupied Dyson orbitals. For completeness, one can also introduce a parallel set of "unoccupied" Dyson orbitals, which connect the ground state to various $(N+1)$ particle states containing an added electron.

The importance of Dyson orbitals in understanding the nature of the Compton scattering spectra beyond the

framework of the IA and the IPM has been emphasized by Kaplan *et al.* [1]. In particular, the triple-differential scattering cross-section for the (γ,$e\gamma$) process, which is the elementary process underlying Compton scattering, is given by

$$\frac{d^3\sigma}{d\omega_2 d\Omega_2 d\Omega_e} = r_0^2(1+\cos^2\theta)\frac{\omega_2}{\omega_1} \times \sum_n |g_n(\mathbf{q})|^2 \delta(\omega_1 - \omega_2 - E_b^{(n)} - \frac{p_n^2}{2m}) \ , \quad (4)$$

where $g_n(\mathbf{q})$ is the Fourier transform of $g_n(\mathbf{r})$, $\mathbf{q}$ is the momentum transfered to the final system, ω_1 and ω_2 are respectively the energies of the photon before and after the collision, and the summation extends over the occupied Dyson orbitals. Eq. (4) assumes a large energy transfer ($\omega_1 - \omega_2 >> E_b^{(n)}$), so that the outgoing electron possesses sufficiently high energy that it can be approximated by a free electron plane wave form. The binding energy $E_b^{(n)}$ in the δ-function in Eq. (4) is usually neglected in obtaining the standard IA-based expression for the cross section. The resulting form of the Compton profile after coordinates of the recoil electron are integrated over can be shown to be symmetric around $q = 0$. Therefore, an accurate computation of the binding energies $E_b^{(n)}$ is important for describing the asymmetry of the Compton profile related to deviations from the IA.

III. GREEN'S FUNCTION METHOD

In order to gain a handle on the nature of the excitation energies $E_b^{(n)}$, it proves useful to approach the problem through the Green's function method. The orbitals $g_n(\mathbf{r})$ of Eq. (1) satisfy the Dyson equation [9, 10, 11]

$$(\frac{p^2}{2m} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}))g_n(\mathbf{r}) + \int d^3\mathbf{r}' \ \Sigma_{xc}(\mathbf{r},\mathbf{r}',E_b^{(n)})g_n(\mathbf{r}') = E_b^{(n)} g_n(\mathbf{r}), \quad (5)$$

where $V_{ext}(\mathbf{r})$ is the external potential, V_H is the Hartree potential and Σ_{xc} is the self-energy.

The Green's function can be expressed as [11]

$$G(\mathbf{r},\mathbf{r}',\omega) = \sum_n \frac{g_n(\mathbf{r})g_n^*(\mathbf{r}')}{\omega - E_b^{(n)} + i\delta \mathrm{sign}(E_b^{(n)} - \mu)}, \quad (6)$$

where μ is the chemical potential and δ is an infinitesimal positive number. The density matrix $\rho(\mathbf{r},\mathbf{r}')$ and the electron density distribution $n(\mathbf{r}) = \rho(\mathbf{r},\mathbf{r})$ are obtained by integrating the spectral function $A(\mathbf{r},\mathbf{r}',\omega)$ over the occupied electronic energies

$$\rho(\mathbf{r},\mathbf{r}') = \int_{-\infty}^{\mu} d\omega A(\mathbf{r},\mathbf{r}',\omega) \ , \quad (7)$$

where the spectral function $A(\mathbf{r},\mathbf{r}',\omega)$ is given by

$$A(\mathbf{r},\mathbf{r}',\omega) = \sum_n g_n(\mathbf{r})g_n^*(\mathbf{r}')\frac{\delta}{\pi[(\omega - E_b^{(n)})^2 + \delta^2]}. \quad (8)$$

The standard calculation of the self-energy Σ_{xc} and the Green's function G proceeds via the many-body perturbation theory (MBPT) [12]. The first order in the MBPT leads to the so-called GW approximation [13] (G stands for the Green's function and W denotes the screened Coulomb interaction). The GW equation for the self-energy is

$$\Sigma_{xc} = iG_0W \ , \quad (9)$$

where G_0 is the 0th order Green's function. The calculation of W usually requires heavy computations of the dielectric function. Here, we will take a shortcut by describing the screening in terms of the pair-correlation function.

Since many-body effects beyond the Hartree approximation are contained in the exchange-correlation energy E_{xc}, we can write

$$E_{xc} = \frac{1}{2}\int_{-\infty}^{\mu} d\omega d^3\mathbf{r}d^3\mathbf{r}'\Sigma_{xc}(\mathbf{r},\mathbf{r}',\omega)A(\mathbf{r},\mathbf{r}',\omega) \ , \quad (10)$$

where the integral is over the occupied states. In the Hartree-Fock limit, the self energy operator is *instantenous*, i.e., $\Sigma_{xc}(\mathbf{r},\mathbf{r}',\omega) = \Sigma_x(\mathbf{r},\mathbf{r}')$. By integrating over ω, ones finds the well known result for the exchange energy E_x [14]

$$E_x = \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}'\Sigma_x(\mathbf{r},\mathbf{r}')\rho(\mathbf{r},\mathbf{r}') \ . \quad (11)$$

We now consider the standard expression of the exchange-correlation energy E_{xc} in terms of the exchange-correlation hole [15]

$$E_{xc} = \frac{1}{2}\int d^3\mathbf{r}d^3\mathbf{r}' \ \int_0^1 d\lambda \frac{n(\mathbf{r})n(\mathbf{r}')C_\lambda(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ , \quad (12)$$

where λ is the coupling constant from the Hellmann-Feynman theorem, and C_λ is a pair-correlation function describing the exchange-correlation hole. The two expressions of Eqs. (10) and (12) for E_{xc} can be linked by assuming a *local* and *instantaneous* ansatz for the self-energy operator [16]

$$\Sigma_{xc}(\mathbf{r},\mathbf{r}',\omega) = 2\epsilon_{xc}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'). \quad (13)$$

Here

$$\epsilon_{xc}(\mathbf{r}) = \frac{1}{2}\int d\mathbf{r}' \int_0^1 d\lambda \frac{n(\mathbf{r})n(\mathbf{r}')C_\lambda(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (14)$$

is the exchange-correlation energy per particle.

Eq.(13) has an intuitive interpretation. When an electron moves, its exchange-correlation hole moves with it

and modifies its effective mass and excitation energy. Insight into the local approximation for Σ_{xc} is provided by considering the homogeneous electron gas. In this case, one obtains

$$\Sigma_{xc}(\mathbf{r}, \mathbf{r}', \omega) = 2\bar{\epsilon}_{xc}\delta(\mathbf{r} - \mathbf{r}'), \tag{15}$$

where $\bar{\epsilon}_{xc}$ is a constant due to the translation invariance of the system. A simple expression for $\bar{\epsilon}_{xc}$ in the metallic density range is given by [17]

$$\bar{\epsilon}_{xc} = -\frac{0.916}{r_s} - \frac{0.127}{\sqrt{r_s}} \text{ Ry}, \tag{16}$$

where the mean interelectronic spacing r_s is obtained via the electron density n by $n(4\pi r_s^3/3) = 1$. Thus, as a consequence of the short range of the self-energy, the electron-electron interaction leads only to a uniform shift of the levels in relation to the non-interacting gas. In the Hartree-Fock case, the density of states unphysically goes to zero at the Fermi level as a result of the long range of the self-energy [14]. The situation in a real metal is presumably closer to that of the homogeneous electron gas as the screening tends to make the correct Σ_{xc} local. Indeed, band calculations based on the Density Functional Theory (DFT) employing local potentials [15] have been rather successful in reproducing the experimental FS's in wide classes of materials [18].

Bearing these considerations in mind, the correction to the excitation energy $E_b^{(n)}$ of Eq. (6) may be obtained in the first perturbational order as

$$E_b^{(n)} = \varepsilon_n + \int d^3\mathbf{r}\ (2\epsilon_{xc}(\mathbf{r}) - v_{xc}(\mathbf{r}))|g_n(\mathbf{r})|^2\ , \tag{17}$$

where ε_n denotes the Kohn-Sham eigenvalue and $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta n(\mathbf{r})$ is the exchange-correlation potential in the Kohn-Sham equations. $g_n(\mathbf{r})$ on the right hand side of Eq. (17) can be reasonably replaced by the Kohn-Sham orbitals [19]. The exchange-correlation energy per particle ϵ_{xc} is computed straightforwardly within the local density approximation (LDA) [15]. Notably, correction to $E_b^{(n)}$ in Eq. (17) will in general be state-dependent and therefore this spectrum will be a useful starting point for implementing the scheme proposed by Barbiellini and Bansil [20] for treating the momentum density and Compton profile of the correlated ground state of the anisotropic electron gas beyond the Lam-Platzman correction.

IV. EXCITATION ENERGY CALCULATIONS

Fig. 1 provides an illustrative example of the usefulness of Eq. (17). The first ionization energy of atoms from H to C ($Z = 1 - 6$) is considered using relativistic DFT atomic wavefunctions [21]. The exchange-correlation energy $\epsilon_{xc}(\mathbf{r})$ and the potential $v_{xc}(\mathbf{r})$ have

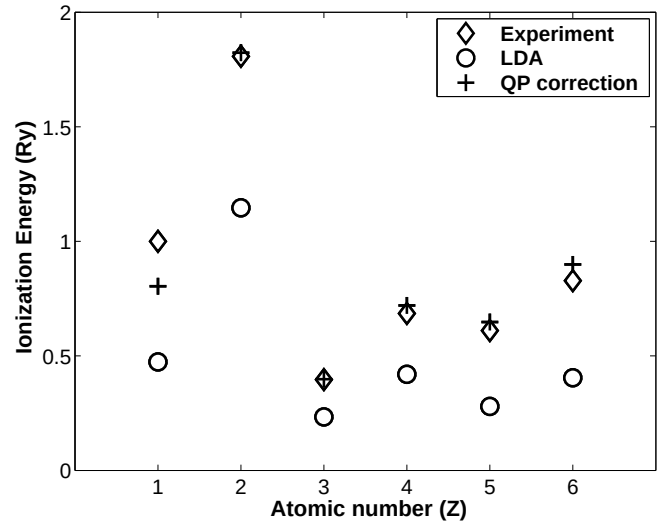

FIG. 1: Comparison of the theoretical and experimental atomic first ionization energies for H ($Z = 1$) to C ($Z = 6$). Diamonds are the experimental values [23], open circles give LDA values, while crosses give values corrected by using Eq. (17).

been calculated within the LDA parametrized by Hedin and Lundqvist [22]. The LDA eigenvalues (open circles) are seen to be substantially lower than the experimental values (diamonds). The quasiparticle correction of Eq. (17) brings the theoretical values (crosses) in substantial agreement with the experimental values [23]. Note that in the case of H, although the quasiparticle correction yields a large improvement, the self-interaction error is not fully removed and about 20 % discrepancy between theory and experiment remains.

We have also applied our scheme to investigate the band gap in diamond. For this purpose, the selfconsistent electronic band structure of diamond [24] was obtained using the local density exchange-correlation functional of Hedin and Lundqvist [22]. As expected, the LDA band gap of 3.99 eV so computed is too small. The inclusion of the correction of Eq. (17) yields a gap of 5.3 eV, which is in far better agreement with the experimental value of 5.48 eV [25]. More generally, we expect our correction to reproduce semiconductor bandgaps with an accuracy comparable to that of the computationally more involved GW approximation [26, 27, 28, 29, 30]. It should also be noted that in analyzing the generalized density-functional theory (GDFT), several authors have pointed out that the energy of electronic excitations across the gap of insulators and semiconductors can be expressed as the sum of the so-called Kohn-Sham gap and a correction that is usually of the same order of magnitude [31, 32, 33].

We note that quasi-particle effects directly influence the shape of the FS of a metal. For instance, the FS of Cu can be measured very precisely so that direct com-

parisons with theoretical predictions are easy to follow. de Hass-van Alphen (dHvA) measurements[34] find the large belly of the FS of Cu to be more spherical compared to the LDA computations. In V, dHvA [35] and positron annihilation [36] experiments indicate that the FS pockets at the N symmetry point are smaller than those from LDA calculations. In γ-Ce, an improved agreement with positron annihilation results is obtained with the LDA FS if the f-band is moved up by $40-50$ mRy [37]. Interestingly, aforementioned discrepancies concerning the FSs can be substantially corrected via a simplified computation of the self-energy via the exchange correlation hole [38].

V. SUMMARY AND CONCLUSIONS

We discuss aspects of Dyson orbitals for gaining insight into quasi-particle effects in the correlated ground state of a many-particle system. The importance of Dyson orbitals, which connect the many-body ground state with its singly ionized excited states, has been emphasized previously for describing Compton scattering profiles beyond the limitations of the IA and the IPM and we start with a brief review of this earlier study [1]. We focus on delineating corrections to the Kohn-Sham energies due to quasi-particle effects and show how one can gain a handle on obtaining substantially improved excitation energies in molecules and solids. For this purpose, a Green's function approach is used to suggest a relatively simple local form of the exchange-correlation energy. Illustrative applications of our scheme indicate that our self-energy expression should provide a reasonable description of excitation energies in metals and semiconductors with an accuracy roughly comparable to that of the GW method.

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