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Electron self-energy in A_3C_{60} (A = K, Rb): effects of t_{1u} plasmons in the GW approximation

O Gunnarsson

Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

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Abstract. The electron self-energy of the t_{1u} states in A_3C_{60} (A = K, Rb) is calculated using the so-called GW approximation. The calculation is performed within a model which considers the t_{1u} charge-carrier plasmon at 0.5 eV and takes into account scattering of the electrons within the t_{1u} band. A moderate reduction (35%) of the t_{1u} band width is obtained.

1. Introduction

The alkali-doped fullerenes A_3C_{60} (A = K, Rb) have a low-energy charge-carrier plasmon at an energy of about 0.5 eV [1–3], which essentially results from the oscillation of the alkali electrons donated to the t_{1u} band. This plasmon has a rather strong coupling to the electrons, and it is believed to play an important role in producing the anomalously large band width seen in angle-integrated photoemission for these systems [4], since it can cause large-binding-energy plasmon satellites.

It is interesting to calculate the electron self-energy due to the coupling to the plasmons, to more generally study the effects of the plasmons on the electronic properties. We here use the so-called GW approximation, where the self-energy is calculated to lowest order in the screened Coulomb interaction [5]. This approximation has been widely applied to the electron gas, free-electron-like systems, and semiconductors. For these systems it is found that the self-energy has a moderate effect on the electron dispersion, and that it can somewhat increase or reduce the effective mass, depending on the system. A_3C_{60}, however, has a quite different band structure to these systems, and it is interesting to ask whether the effective mass and the width of the band might be more strongly modified in this system.

This issue is, for instance, raised by the results for the optical conductivity. Experimentally, the Drude peak is very narrow [6], perhaps an order of magnitude narrower than predicted by a one-particle theory [7]. This may suggest that the effective mass is greatly enhanced in A_3C_{60}. On the other hand, the specific heat has been estimated to be small [8], perhaps even smaller than would have been expected from band-structure calculations [9], suggesting that the effective mass is not strongly renormalized, and perhaps even somewhat reduced. The coupling to phonons with the coupling constant λ_{ph} reduces the dispersion by a factor of $1/(1 + \lambda_{ph})$. If this result is directly taken over for the plasmons, we may estimate a coupling constant $\lambda_{pl} \sim 2.5$, and a substantial reduction (more than a factor of three) of the dispersion.

The coupling to a plasmon studied here corresponds to the GW method in the plasmon pole approximation, which was first introduced and extensively studied by Lundqvist *et al* [10] and later by Overhauser [11] for the electron gas. Shirley and Louie have applied the

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GW approximation to solid C_{60} [12]. Since they considered undoped C_{60}, the t_{1u} plasmon considered here did not enter their calculation, while the contribution to the self-energy in their calculation (a plasmon at about 25 eV) is not included in the model used below. The two calculations are therefore complementary, and address different parts of the physics of A_3C_{60}.

The coupling to the plasmon leads to a so-called plasmaron satellite in the spectral function, where a plasmon has been excited [10]. This satellite is obtained in the *GW* approximation [10], but a more accurate treatment would also give higher satellites with several plasmons excited [13, 14]. These higher plasmon satellites are believed to be important for the broad spectrum seen in angle-integrated photoemission for A_3C_{60} [4, 15]. The *GW* approximation can therefore not be expected to give an accurate spectrum in the satellite region. We also observe that the Coulomb interaction U between two electrons on the same C_{60} molecule is large compared with the t_{1u} band width W [16], which suggests that many-body effects beyond the *GW* approximation may be important. For instance, a proper treatment of the threefold degeneracy of the t_{1u} orbital is important for understanding why these systems are not Mott–Hubbard insulators, in spite of the large value of U/W [17]. The *GW* results for A_3C_{60} should therefore be treated with a certain caution, but it is still interesting to see whether a strong renormalization of the band width is obtained.

In section 2 we present the formalism, and in section 3 the model used in these calculations. The results are presented in section 4, and discussed in section 5.

2. Formalism

We write the dielectric function of A_3C_{60} as

$$\epsilon(\boldsymbol{q},\omega) = \epsilon_0 - \frac{\omega_{0p}^2}{m^*\omega^2} \tag{1}$$

where ϵ_0 is the contribution to ϵ due to all excitations in the system except the ones inside the t_{1u} band. Since most of these excitations have a rather high energy relative to the energy scale of interest here (the t_{1u} band width), we assume ϵ_0 to be energy independent. The second term describes the excitations inside the t_{1u} band. ω_{0p} is the plasmon frequency one would deduce for free electrons with the same density as the t_{1u} electrons, and m^* is the band mass of the t_{1u} electrons. The value of ω where $\epsilon(\boldsymbol{q},\omega) = 0$ gives the plasmon frequency

$$\omega_p = \frac{\omega_{0p}}{\sqrt{m^*\epsilon_0}}. \tag{2}$$

Above, we have neglected local-field effects as well as the $\boldsymbol{q}$-dependence of ϵ_0. Neither approximation is quite justified [2]. Thus the $\boldsymbol{q}$-dependence of ϵ_0 tends to give ω_p a positive dispersion, while the local-field effects tend to give a negative dispersion. As far as the plasmon frequency is concerned, however, these two effects essentially cancel, in agreement with the experimental observation that ω_p has a negligible dispersion [2]. Equations (1) and (2) therefore give a good description of the plasmon frequency, but neglect the substantial broadening of the plasmon [3].

For K_3C_{60}, the t_{1u} electron density corresponds to the electron gas density parameter $r_s = 7.3a_0$ and $\omega_{0p} = 2.4$ eV. In an electron gas of this density, the occupied part of the band is about 0.9 eV, while the calculated full band width of K_3C_{60} is about 0.6 eV [9]. This corresponds to $m^* \sim 0.9/(0.6/2) = 3$. At $\boldsymbol{q} = 0$, $\epsilon_0 \sim 4.4$ [18]. We then find that $\omega_p \sim 0.66$ eV. This is somewhat larger than the experimental result, $\omega_p \sim 0.5$ eV [2], which will be used in the following.

The self-energy is in the GW approximation written as [5]

$$\Sigma_{nn'}(\boldsymbol{k},\omega) = \mathrm{i}\sum_{\boldsymbol{k}'n''}\int \frac{\mathrm{d}\omega'}{2\pi}\,\frac{U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}')}{\epsilon(\omega')}\,\frac{\mathrm{e}^{\mathrm{i}\omega' 0^+}}{\omega+\omega'-\varepsilon_{\boldsymbol{k}'n''}+\mu_0} \tag{3}$$

where $U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}')$ is the Coulomb matrix element connecting the Bloch states $|\boldsymbol{k}n\rangle$ and $|\boldsymbol{k}'n''\rangle$ with the argument $\boldsymbol{r}$, and $|\boldsymbol{k}n'\rangle$ and $|\boldsymbol{k}'n''\rangle$ with the argument $\boldsymbol{r}'$. Here $\boldsymbol{k}$ is a wave vector and n a band index. 0^+ is a positive infinitesimal number, which ensures the proper behaviour for large ω'. $\varepsilon_{\boldsymbol{k}'n''}$ is the noninteracting energy of the state $|\boldsymbol{k}'n''\rangle$, and μ_0 is an average of the self-energy over the Fermi surface. We split the dynamically screened Coulomb interaction U/ϵ in two parts:

$$\frac{U}{\epsilon(\omega)} = \frac{U}{\epsilon_0} + \frac{\omega_p U}{2\epsilon_0}\frac{2\omega_p}{\omega^2-\omega_p^2}. \tag{4}$$

The first term then gives a statically screened exchange contribution to the self-energy:

$$\Sigma^x_{nn'}(\boldsymbol{k},\omega) = -\frac{1}{\epsilon_0}\sum_{\boldsymbol{k}'n''}^{\mathrm{occ}} U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}') \tag{5}$$

while the second part gives a correlation contribution. We can interpret $2\omega_p/(\omega^2-\omega_p^2)$ in equation (4) as a boson Green's function, and

$$g^2_{nn'',n'n''}(\boldsymbol{q}) = \frac{\omega_p}{2\epsilon_0}U_{nn'',n'n''}(\boldsymbol{q}) \tag{6}$$

as a coupling constant, in analogy with previous work [10]. Closing the integration contour in the upper half of the complex ω'-plane, we obtain the correlation contribution to the self-energy:

$$\Sigma^c_{nn'}(\boldsymbol{k},\omega) = \frac{\omega_p}{2\epsilon_0}\sum_{\boldsymbol{k}'n''}^{\mathrm{occ}}\frac{U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}')}{\omega-\varepsilon_{\boldsymbol{k}'n''}+\mu_0+\omega_p} + \frac{\omega_p}{2\epsilon_0}\sum_{\boldsymbol{k}'n''}^{\mathrm{unocc}}\frac{U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}')}{\omega-\varepsilon_{\boldsymbol{k}'n''}+\mu_0-\omega_p}. \tag{7}$$

3. The model

We consider a model with three t_{1u} orbitals. The hopping matrix elements connecting these orbitals have been described in a tight-binding parametrization [19, 20], which is used here. This parametrization is used to calculate the noninteracting band-structure energies $\varepsilon_{\boldsymbol{k}n}$, and wave functions

$$\psi_{\boldsymbol{k}n}(\boldsymbol{r}) = \sum_{\nu=1}^{3} c_\nu^{(n)}\phi_{\boldsymbol{k}\nu}(\boldsymbol{r}) \tag{8}$$

where

$$\phi_{\boldsymbol{k}\nu}(\boldsymbol{r}) = \frac{1}{\sqrt{N}}\sum_{j=1}^{N}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_j}\Phi_\nu(\boldsymbol{r}-\boldsymbol{R}_j) \tag{9}$$

is a Bloch state of a t_{1u} molecular orbital $\Phi_\nu(\boldsymbol{r})$. There are N molecules with the coordinates $\boldsymbol{R}_j$.

We further have to specify the matrix elements of the Coulomb interaction. We assume that

$$\int \mathrm{d}^3r \int \mathrm{d}^3r'\ \Phi_{\nu_1}(\boldsymbol{r}-\boldsymbol{R})\Phi_{\nu_2}(\boldsymbol{r}-\boldsymbol{R})\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\Phi_{\nu_3}(\boldsymbol{r}'-\boldsymbol{R}')\Phi_{\nu_4}(\boldsymbol{r}'-\boldsymbol{R}')$$

$$= \delta_{\nu_1\nu_2}\delta_{\nu_3\nu_4} \times \begin{cases} \dfrac{e^2}{|\boldsymbol{R}-\boldsymbol{R}'|} & \text{if } \boldsymbol{R} \neq \boldsymbol{R}' \\ U_0 & \text{if } \boldsymbol{R} = \boldsymbol{R}'. \end{cases} \tag{10}$$

For the Coulomb matrix elements connecting Bloch states we then find

$$\langle \boldsymbol{k}\nu_1\boldsymbol{k}'\nu_2|\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}|\boldsymbol{k}\nu_3\boldsymbol{k}'\nu_4\rangle = \frac{1}{N}\left(U_0 + \sum_{\boldsymbol{R}\neq 0}\frac{\mathrm{e}^{\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{R}}}{|\boldsymbol{R}|}\right)\delta_{\nu_1\nu_2}\delta_{\nu_3\nu_4}. \tag{11}$$

We replace the sum over $\boldsymbol{R}$ by an integral over all space outside a Wigner–Seitz sphere with the radius $R_0 = 5.56$ Å. This gives

$$\langle \boldsymbol{k}\nu_1\boldsymbol{k}'\nu_2|\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}|\boldsymbol{k}\nu_3\boldsymbol{k}'\nu_4\rangle = \frac{1}{N}\left[U_0 + \frac{4\pi e^2}{\Omega|\boldsymbol{k}-\boldsymbol{k}'|^2}\cos(R_0|\boldsymbol{k}-\boldsymbol{k}'|)\right]\delta_{\nu_1\nu_2}\delta_{\nu_3\nu_4} \tag{12}$$

where Ω is the volume of the Wigner–Seitz cell. We have put $U_0 = 4$ eV, using a simple estimate based on the radius of the C_{60} molecule. Alternatively, we can extend the integration over R over all space, putting $R_0 = 0$. In this case we should put $U_0 = 0$ to avoid double counting.

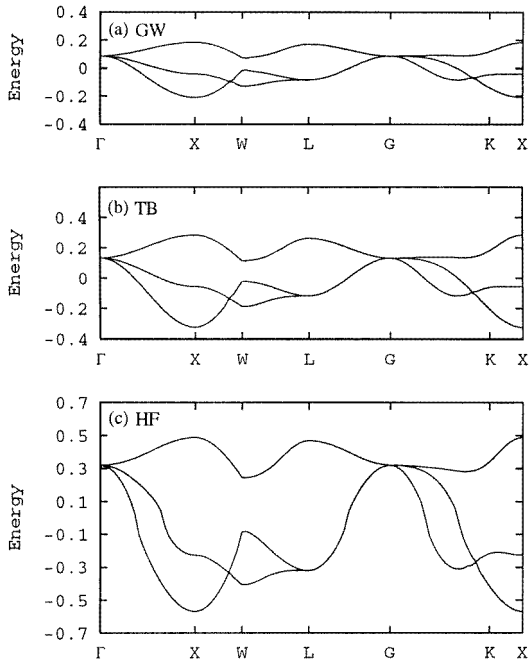

Figure 1. The quasi-particle (GW) (a) band structure for the t_{1u} band compared with the noninteracting tight-binding (TB) (b) and Hartree–Fock (HF) (c) band structures. Relative to the TB band structure, the GW band width is reduced by about 35%, while the HF width is increased by about 75%.

4. Results

We have calculated the self-energy as described above. The quasi-particle energy E_{kn} is obtained by solving the equation

$$E_{kn} = \varepsilon_{kn} + \Sigma(\boldsymbol{k}, E_{kn}) \tag{13}$$

where ε_{kn} is the band-structure energy. We can also obtain the quasi-particle weight as

$$Z_{kn} = \frac{1}{1 - \delta\Sigma(\boldsymbol{k}, \omega)/\delta\omega} \tag{14}$$

where the derivative is evaluated at the quasi-particle energy. The resulting quasi-particle (GW) band structure is compared with the noninteracting tight-binding (TB) and Hartree–Fock (HF) band structures in figure 1. The figure shows a moderate reduction (∼35%) of the GW band width relative to the TB width, while the HF band width is almost a factor of two larger (75%) than the TB result.

The quasi-particle strength is relatively small, $Z \sim 0.4$–0.5. This is smaller than what is found in electron gas calculations at metallic densities. Since the three t_{1u} electrons correspond to a very low density with $r_s \sim 7$, this small value of Z is, however, not very surprising. Actually, extrapolation of earlier [5] GW calculations for the electron gas to $r_s = 7.3$ suggest $Z \sim 0.52$. The small value of Z implies that a substantial spectral weight is transferred to satellites.

Replacing $U_0 = 4$ eV and $R_0 = 5.56$ Å in the model (12) by $U_0 = 0$ and $R_0 = 0$, e.g., a pure $1/q^2$ interaction, gives a small change of the quasi-particle band structure. This suggests that the results are not very sensitive to the details of the model.

5. Discussion

The results in figure 1 illustrate that there is a large cancellation between the exchange and correlation effects. This is also observed in the electron gas, although in that case the cancellation is more complete than here [5, 10].

Of particular interest is the energy dependence of the self-energy. For the sake of the discussion, we neglect the $\boldsymbol{q}$-dependence of the coupling constant $g(\boldsymbol{q})$ (equation (6)) and replace it by its average over the Brillouin zone. We further assume that the plasmons couple to a nondegenerate band of width $2B$ and with a constant density of states. The correlation part of the self-energy is then given by (equations (7))

$$\text{Re } \Sigma_0^c(\omega) = \frac{\lambda\omega_p}{2}\left[\ln\left|\frac{\omega + B + \omega_p}{\omega + \omega_p}\right| + \ln\left|\frac{\omega - \omega_p}{\omega - B - \omega_p}\right|\right] \tag{15}$$

where

$$\lambda = \frac{2g^2}{\omega_p}N(0) = \frac{g^2}{\omega_p B} \tag{16}$$

is a coupling constant defined as for the electron–phonon coupling, and $N(0) = 1/(2B)$ is the density of states. In the present case, we have $\lambda \sim 2.5$. In the limit $|\omega| \ll \omega_p \ll B$, we have

$$\text{Re}\Sigma_0^c(\omega) = -\lambda\omega \qquad |\omega| \ll \omega_p \ll B. \tag{17}$$

In the opposite limit where $\omega_p \gg B, |\omega|$, we have

$$\text{Re } \Sigma_0^c(\omega) = -\left(\frac{g}{\omega_p}\right)^2\omega \qquad |\omega|, B \ll \omega_p. \tag{18}$$

The coupling constant $(g/\omega_p)^2 \sim 1.4$ in the present case. The 'phonon'-like formula in equation (17) predicts that the quasi-particle weight is $Z \sim 0.29$, while the formula (18) predicts $Z \sim 0.42$. The latter result fits the actual calculations nicely—not too surprisingly in view of the parameter range considered here ($\omega_p = 0.5$ eV, $B = 0.3$ eV). The fact that the system is not in the 'phonon' parameter range ($\omega_p \ll B$) therefore means that correlation effects lead to a less drastic narrowing of the band. This narrowing is furthermore to a substantial degree compensated by exchange effects.

Nevertheless, the narrowing of the band is larger than found in the GW approximation for the electron gas at metallic densities. We want to discuss this further.

We rewrite the self-energy as

$$\Sigma^{xc}_{nn'}(\boldsymbol{k},\omega) = -\frac{1}{2\epsilon_0}\sum_{\boldsymbol{k}'n''} U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}') - \frac{1}{2\epsilon_0}\sum_{\boldsymbol{k}'n''}^{\text{occ}} \frac{U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}')(\omega - \varepsilon_{\boldsymbol{k}'n''} + \mu_0)}{\omega - \varepsilon_{\boldsymbol{k}'n''} + \mu_0 + \omega_p}$$
$$-\frac{1}{2\epsilon_0}\sum_{\boldsymbol{k}'n''}^{\text{unocc}} \frac{U_{nn'',n'n''}(\boldsymbol{k}-\boldsymbol{k}')(\omega - \varepsilon_{\boldsymbol{k}'n''} + \mu_0)}{\omega - \varepsilon_{\boldsymbol{k}'n''} + \mu_0 - \omega_p}. \tag{19}$$

In the first term the sum is over the whole Brillouin zone, and it can therefore be shown that within the model in equation (12) it is state independent. We can then focus on the next two terms. If ω_p is very large, these two terms go to zero. The band is then just shifted to lower energies, without any change in shape or width. We next consider finite values of ω_p, but for a moment we assume that ω_p is still larger than the band width. If $\omega + \mu_0$ is put at the bottom of the band, both terms are then positive for all $\boldsymbol{k}''$. States at the bottom of the band are then pushed upwards by the last two terms. In the same way, states at the top of the band are pushed downwards, leading to a narrowing of the band. These arguments are not qualitatively different if ω_p is somewhat smaller than the noninteracting band width. Some of the energy denominators in equation (19) could become negative, but the effect of reducing ω_p tends to be a further reduction of the band width. We observe that these arguments are specific to this model, where we have assumed that the states have not just a lower bound but also an upper bound. For the electron gas and most other systems there is no upper bound, and no definite statements of this type can be made.

In the calculation above, we have only considered the coupling to the t_{1u} charge-carrier plasmon, and neglected the coupling to, e.g., the plasmon at about 25 eV as well as the exchange interaction with all occupied states except the t_{1u} states. These effects were considered in the calculation by Shirley and Louie [12], who found a broadening of the t_{1u} band by about 30%. If this broadening is added to our results, we find an essentially unchanged t_{1u} band width. This result can then not explain the narrow Drude peak in the optical conductivity, but it is essentially consistent with the rather small specific heat deduced for these systems.

References

[1] Sohmen E, Fink J and Krätschmer W 1992 *Europhys. Lett.* **17** 51
[2] Gunnarsson O, Eyert V, Knupfer M, Fink J and Armbruster J F 1996 *J. Phys.: Condens. Matter* **8** 2557
[3] Liechtenstein A I, Gunnarsson O, Knupfer M, Fink J and Armbruster J F 1996 *J. Phys.: Condens. Matter* **8** 4001
[4] Knupfer M, Merkel M, Golden M S, Fink J, Gunnarsson O and Antropov V P 1993 *Phys. Rev.* B **47** 13 944
[5] Hedin L 1965 *Phys. Rev.* **139** A796
[6] Degiorgi L 1995 *Mod. Phys. Lett.* B **9** 445
[7] van den Brink J, Gunnarsson O and Eyert V 1997 to be published
[8] Burkhart G J and Meingast C 1996 *Phys. Rev.* B **54** R6865
[9] Gunnarsson O 1997 *Rev. Mod. Phys.* **69** 575

[10] Lundqvist B I 1967 *Phys. Kondens. Mater.* **6** 193
Lundqvist B I 1967 *Phys. Kondens. Mater.* **6** 206
Hedin L, Lundqvist B I and Lundqvist S 1967 *Int. J. Quantum Chem.* **IS** 791
[11] Overhauser A W 1971 *Phys. Rev.* B **3** 1888
[12] Shirley E L and Louie S G 1993 *Phys. Rev. Lett.* **71** 133
[13] Langreth D 1970 *Phys. Rev.* B **1** 471
[14] Hedin L 1980 *Phys. Scr.* **21** 477
[15] Gunnarsson O, Meden V and Schönhammer K 1994 *Phys. Rev.* B **50** 10 462
[16] Lof R W, van Veenendaal M A, Koopmans B, Jonkman H T and Sawatzky G A 1992 *Phys. Rev. Lett.* **68** 3924
[17] Gunnarsson O, Koch E and Martin R M 1996 *Phys. Rev.* B **54** R11 026
[18] Hebard A F, Haddon R C, Fleming R M and Kortan R 1991 *Appl. Phys. Lett.* **59** 2109
[19] Gunnarsson O, Satpathy S, Jepsen O and Andersen O K 1991 *Phys. Rev. Lett.* **67** 3002
[20] Satpathy S, Antropov V P, Andersen O K, Jepsen O, Gunnarsson O and Liechtenstein A I 1992 *Phys. Rev.* B **46** 1773