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New Journal of Physics (ISSN: 1367-2630)

Citation for the published paper:
Monreal, R. ; Antosiewicz, T. ; Apell, S. (2013) "Competition between surface screening and size quantization for surface plasmons in nanoparticles". New Journal of Physics, vol. 15

http://dx.doi.org/10.1088/1367-2630/15/8/083044

New Journal of Physics
The open access journal for physics

Competition between surface screening and size quantization for surface plasmons in nanoparticles

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New Journal of Physics **15** (2013) 083044 (10pp)
Received 2 June 2013
Published 22 August 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/8/083044

Abstract. We present a theoretical model for analyzing the size dependence of the surface plasmon resonance of metallic nanospheres in a range of sizes down to a single nanometer. Within this model, we explicitly show how different microscopic mechanisms, namely quantization due to size (quantum size effect (QSE)) and dynamical surface screening, affect the energy of the surface plasmon. We demonstrate that the latter mechanism, which can move the surface plasma energy both toward the red or the blue, can be comparable to or even stronger than QSE. Thus, depending on material parameters, QSE may only be observed for ultra-small metal nanoparticles much closer to 1 nm in size than to 10 nm. Results presented herein are in quantitative agreement with recent published experimental results for Ag and Au.

During the last 20 years, there has been considerable progress in both calculating and measuring the properties of ultra-small particles [1–5] as well as the corresponding efforts for clusters. Of particular interest is to monitor the region where cluster research meets and merges with the corresponding small particle research [6–9]. Furthermore, in the last few years, the behavior

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of plasmon resonances in nanosystems has become a hot topic for its important applications in varied fields ranging from cancer therapy, nanophotonic devices, biosensing to catalysis. Interesting physical aspects of these resonances include, among others, investigation of the quantum regime of tunneling plasmonics [10, 11] or what is an ultimate limit to electromagnetic enhancement in these systems [12, 13]. In spite of all this effort, several aspects of the behavior of plasmon resonances in nanometer-sized metallic spheres are not fully understood. A particularly interesting example concerns the energy shift experienced by the surface plasmon as a function of the size and shape of the particle. There has been in the literature a variety of experimental reports of *blueshifts* [9, 14–20] or *redshifts* [7, 21] of these resonances as the particle dimensions are reduced, which today may seem conflicting. There have, of course, been many attempts over the years to address this question theoretically [16, 22–26]. However, it is only recently that the experimental situation has become so well controlled that a realistic comparison can be made with theoretical model predictions.

The classical Mie electromagnetic theory [27] is adequate for describing the optical properties of particles with a radius larger than 10 nm. Its main ingredient is the frequency-dependent dielectric function $\epsilon(\omega)$ of the material and its most characteristic feature is the presence of a surface plasmon resonance. The resonance moves in energy as the particle size is changed, depending on the value of the radius R with respect to the effective wavelength of the plasmon c/ω_p, where c is the speed of light and ω_p is the plasma frequency of the volume plasmon. The Mie theory gives rise to saturation of this energy at the value $\omega_\mathrm{s}^\mathrm{cl} = \omega_\mathrm{p}/\sqrt{1+2\epsilon_\mathrm{m}}$ for radii smaller than the wavelength, where ϵ_m is the dielectric constant of the medium surrounding the particle (assumed to be frequency independent). When dealing with particles in the size range 1–10 nm, the surface starts to become important compared with the bulk response and thus influences heavily collective modes localized in the surface region. Then one cannot ignore the non-locality of the dielectric response, which requires a microscopic description of the electronic motion in the presence of external fields. This description will in turn condition the screening properties of the electronic system, particularly at metal surfaces. Therefore, a theory of surface screening beyond the classical model is necessitated by non-locality. (For a thorough discussion of this issue, we refer the reader to the review paper by Feibelman [28], where a detailed comparison of the results of different non-local models is made.) Since electrons are able to spill out of the metal because of the finite potential barrier at the surface, the surface screening of an external perturbation is drastically changed from the Mie model assuming, as it does, a sharp interface between a particle and the surrounding medium. Whereas the classical theory is characterized by bulk dielectric properties and thus the length scale R (the particle radius), the surface enters the electrodynamic response as a frequency-dependent complex length scale $d_r(\omega)$ [29] to be introduced below. Reducing the radius below a few nanometers, we move to a region where again the bulk becomes important in a new fundamental way by entering the quantum size effect (QSE) region where the discrete energy level spectrum makes it possible to set up standing electron–hole pairs and quantum core plasmons [1, 5]. The last are charge oscillations localized at the very center of the particle because of the quantum confinement of the electrons. These QSEs influence the particle response to a significant degree and compete with the effect coming from the surface. For these ultra-small particles, sophisticated time-dependent density functional theory (TDDFT) and time-dependent local density approximation (TDLDA) calculations are available nowadays [1, 2, 5, 9, 11, 18]. However, these become increasingly computationally demanding with increasing radius.

The purpose of this paper is to analyze the role of different microscopic mechanisms affecting the energy of the surface plasmon of metallic spheres as a function of their size, for diameters going down to a few nanometers. To do so, we present a theoretical model, based on known concepts of dynamical surface screening (known in the literature as the surface spill-out effect) and QSEs, which successfully bridges cluster (sub 1 nm) research and Mie theory (greater than 10 nm) predicting results that agree with TDDFT calculations. Our work is triggered by very detailed experiments, recently available [19, 20] which greatly improve the possibilities of checking basic electromagnetic response theory predictions with experimental findings. In passing, we note that the theoretical framework used in these papers does not appropriately include the major effect of the surface spill-out electrons, thus giving the reader the impression that quantum effects start to enter the picture for diameters much larger than they actually do. We find that electron spill-out effects, which can move the surface plasma energy both toward the red or the blue, can be comparable to or even stronger than QSE. We show that, by properly taking into account surface screening and d-electrons, the experimental surface plasmon energies of Ag and Au particles in a variety of host media can be reproduced down to a few nm sized particles and the discrepancy at smaller sizes can be accounted for in a simple model of QSEs.

The electromagnetic response of a particle in dipolar approximation can be described by its polarizability. In this approximation, non-local surface effects can be included in the polarizability by means of general arguments relating the power absorbed by the sphere with the distribution of the electric field at its surface via the induced charge density. The polarizability of a metal sphere of radius R with a bulk dielectric constant $\epsilon(\omega)$ can be written as [29–31]

$$\alpha(\omega) = R^3 \frac{(\epsilon(\omega) - \epsilon_\mathrm{m})\left(1 - \frac{d_r(\omega)}{R}\right)}{\epsilon(\omega) + 2\epsilon_\mathrm{m} + 2\left(\epsilon(\omega) - \epsilon_\mathrm{m}\right)\frac{d_r(\omega)}{R}}, \tag{1}$$

where the length $d_r(\omega)$ is related to the charge density, $\delta\rho(r,\omega)$, induced by the external perturbation, by the formula

$$\frac{d_r(\omega)}{R} = \frac{\int \mathrm{d}r\, r(R-r)\delta\rho(r,\omega)}{\int \mathrm{d}r\, r^2\delta\rho(r,\omega)}, \tag{2}$$

where r is the radial coordinate and the integrals extend to the whole space. The non-local electrodynamic response enters in this formulation through the complex length $d_r(\omega)$. Its real part is a measure of the center of gravity of the screening charge induced in the particle by an external perturbation of frequency ω and its imaginary part describes surface absorption. Note that for the Mie model, where the induced charge density is right at $r = R$, d_r is identically zero and equation (1) reduces to the classical Mie result when retardation is neglected. In this work, we define R as the radius of a sphere containing the total positive charge of the system uniformly distributed in its volume. We will focus in this paper on the shift in energy of the surface plasma resonance, which can be obtained from the poles of the polarizability. Then, from equation (1), the frequency of the surface plasmon resonance, ω_s, has to fulfill

$$\mathrm{Re}\left[\epsilon(\omega_\mathrm{s}) + 2\epsilon_\mathrm{m} + 2(\epsilon(\omega_\mathrm{s}) - \epsilon_\mathrm{m})\frac{d_r(\omega_\mathrm{s})}{R}\right] = 0. \tag{3}$$

It has been known long since [32–37] that the calculated energies of the surface plasmons are very much dependent on the shape of the barrier that confines the electronic system, even for semi-infinite metals. Infinite barrier models confining the electrons inside the metal produce frequencies higher than the classical value while realistic surface barriers can produce lower frequencies because electrons are allowed to spill out of the metal, thus lowering the plasma frequency. The same happens for nanospheres. If electrons are allowed to spill out of the metal, the induced surface charge density has, in general, its main weight outside the surface with its center of gravity giving $\mathrm{Re}\,[d_r(\omega)] < 0$, while a positive value of $\mathrm{Re}\,[d_r(\omega)]$ is obtained if electrons spill in. From equation (3), the *color* of the shift of the surface plasmon frequency with respect to $\omega_\mathrm{s}^\mathrm{cl}$ is directly related to the sign of $\mathrm{Re}\,[d_r(\omega_\mathrm{s})]$: blue and red for positive and negative signs, respectively. Consequently, theoretical models in which the electrons in the nanoparticle are confined directly or indirectly by an infinite barrier [19, 20, 38] can only produce blueshifts. Recently, the so-called non-local hydrodynamical Drude model is being very much used to describe plasmonic nanostructures [39–42]. In this model, the motion of the electrons obeys a linearized Navier–Stokes equation with the electromagnetic field acting as the driving force. Its main advantage is that it is simple, even analytical and can thus be used for different geometries and in cases where retardation is important. It certainly provides insight into the physics that emerges from non-local effects. However, the model has several drawbacks [28], one of them being that it has to be implemented with additional boundary conditions [41]. Moreover, this, like the so-called specular reflection model, invariably yields blue-shifted surface plasmon resonances [39–41] whereas more realistic models based on TDDFT or TDLDA can yield red shifts [2, 5, 11].

The above considerations refer to surface effects. Now we analyze QSEs which are also present at the nanoscale size of interest here. These effects can be described approximately by a dielectric constant similar to the one of a semiconductor: the discrete nature of the electronic states requires a minimum of energy to excite an electron, which is equivalent to having an energy gap. Inspired by the Penn dielectric function for semiconductors [43], we propose to use the following form of the real part of the dielectric function:

$$\epsilon(\omega) = 1 - \frac{\omega_\mathrm{p}^2}{\omega^2 - \Delta^2}, \tag{4}$$

where, as introduced by Gorkov and Eliashberg [44], the energy gap Δ scales with the particle radius as $\Delta = \omega_\mathrm{p} R_0/R$. Using a simple box model, one obtains from their treatment $R_0^2 = \frac{3\pi\hbar^2}{4me^2k_\mathrm{F}}$, where m and e are the electronic mass and charge, respectively, and k_F is the Fermi wave vector. Then in this model R_0 can be written in terms of the effective free-electron density parameter r_s as $R_0 \simeq 1.1 a_0\sqrt{r_\mathrm{s}}$, with a_0 being the Bohr radius. The existence of an energy gap influences the collective modes of the sphere. The classical bulk plasma frequency, given by $\epsilon(\omega) = 0$, depends on the radius R as

$$\omega_\mathrm{p}(R) = \omega_\mathrm{p}\sqrt{1 + \left(\frac{R_0}{R}\right)^2} \tag{5}$$

and, in the absence of any surface effect, the frequency of the surface plasmon changes to

$$\omega_\mathrm{s}(R) = \omega_\mathrm{s}^\mathrm{cl}\sqrt{1 + (1 + 2\epsilon_\mathrm{m})\left(\frac{R_0}{R}\right)^2}. \tag{6}$$

That is, QSE will produce a blueshift of both surface and bulk plasmon energies. We note that the relative shift is larger for the surface compared to the bulk plasmon.

Consequently, in a real situation with both quantum and surface barrier effects present, there is competition between the blue- and the redshifts. Hence, in this work, we apply the two just outlined models to calculate surface plasmon energies in small particles, which will be compared with the experimental results published in [18, 19, 45]. Since we will be dealing with the noble metals Ag and Au, we also need to include the screening due to the d-electrons by modifying equation (4) as

$$\epsilon(\omega) = \epsilon_{\mathrm{d}}(\omega) - \frac{\omega_{\mathrm{p}}^2}{\omega^2 - \Delta^2}, \tag{7}$$

where $\epsilon_{\mathrm{d}}(\omega)$ is obtained from the experimental optical data [46]. This form of $\epsilon(\omega)$ is then introduced into equation (3) to take into account QSEs and d-electrons on the surface plasmon frequency, and we find that it has to fulfill

$$\omega_{\mathrm{s}}^2 = \omega_{\mathrm{p}}^2 \left[\left(\frac{R_0}{R} \right)^2 + \frac{1 + 2\mathrm{Re}\left[\frac{d_r(\omega_{\mathrm{s}})}{R}\right]}{\epsilon_{\mathrm{d}}(\omega_{\mathrm{s}}) + 2\epsilon_{\mathrm{m}} + 2(\epsilon_{\mathrm{d}}(\omega_{\mathrm{s}}) - \epsilon_{\mathrm{m}})\mathrm{Re}\left[\frac{d_r(\omega_{\mathrm{s}})}{R}\right]} \right]. \tag{8}$$

From equation (8), it is clear that QSE, as described by the first term on the right-hand side, will dominate the shift of the surface plasmon frequency at small R while the second term, describing the spill-out effect, will be the most important at a large radius. Therefore, there is a range of values of R where both effects can compete, as we will see below.

In the detailed treatment above, we looked at the center of gravity of the induced density d_r. We now ask what is the influence of d-electrons and QSEs directly on d_r. We can do this to the lowest order by looking at the corresponding quantity for a planar surface $d_\perp(\omega)$ because it has been shown [1] that the induced charge density at the surface of a sphere is very similar to that of a planar surface down to a few nanometers in size. Also, we note that the d-electrons are very localized and therefore largely excluded from the surface region where the conduction electrons spill out [47, 48]. Hence, we will use the values of $d_\perp(\omega)$ calculated by Feibelman [28] for a planar jellium surface of $r_{\mathrm{s}} = 3$ ($r_{\mathrm{s}} = 3.02$ and 3.01 are the values giving the density of conduction electrons in Ag and Au, respectively). However, the screening of the d-electrons is very important in bulk; in particular, it affects the bulk plasma frequency by changing ω_{p} from its free-electron value of 9.1 eV to $\omega_{\mathrm{p}}^* = 3.81$ and 5.99 eV for Ag and Au, respectively. Since $d_\perp$ only depends on the ratio $\omega/\omega_{\mathrm{p}}$, we use for d_r the values of $d_\perp$ with ω renormalized to ω_{p}^*. Then we introduce the effects of d-electrons and of size quantization on d_r through $\omega_{\mathrm{p}}^*(R)$. We would like to point out that the values of d_r we are using result from a full quantum mechanical calculation of the non-local, dynamical surface response function of a planar jellium surface in which the electrons are confined by the Lang–Kohn potential barrier and the electron–electron interactions are considered in a self-consistent field approximation.

We apply equation (8) to calculate the energies of the surface plasmon resonances of three different metals: Ag, Au and a pure free-electron-metal of $r_{\mathrm{s}} = 3$. These metals have in common their close values of the effective free-electron density parameter r_{s}. However, the screening caused by the d-electrons is very different in Ag, Au and a free-electron metal at the typical frequencies of the surface plasmons. This is a crucial physical property for making the resonances of metal nanoparticles shift to different colors. Also, since R_0 and d_r are both of the same order (a few tenths of nm), the relative contributions of surface dynamical screening and QSE depend on $\epsilon_{\mathrm{d}}(\omega_{\mathrm{s}})$.

Figure 1 shows the calculated frequencies of the surface plasmons of Ag nanospheres as a function of the diameter, together with the experimental results by Scholl *et al* [19] for

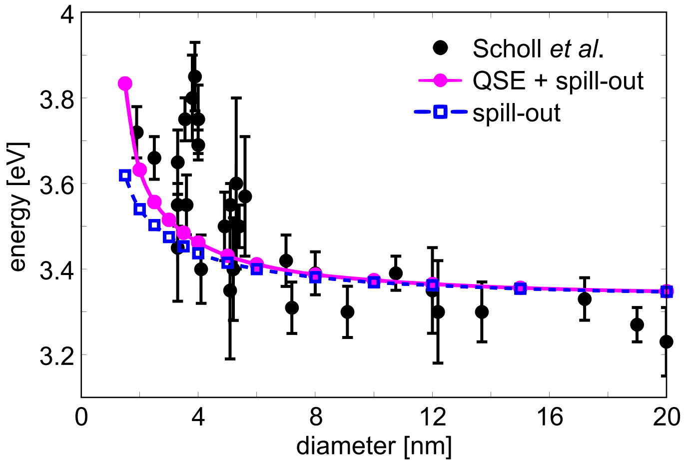

Figure 1. Surface plasmon energy versus diameter for small Ag nanospheres. Points with error bars are experimentally extracted results from electron energy loss spectroscopy (EELS) measurements by Scholl *et al* [19]. The blue line is our calculation of the surface plasmon energy shift resulting from electron spill-out and the magenta line includes the also effects of size quantization. It is clear that the blue line gives a reasonable account for the data, but the magenta line shows an even better agreement with the experiment. It has earlier been claimed that quantum effects start already at 10 nm; however, our calculations show that they do not dominate until the particles are about ten times smaller.

Ag spheres deposited on carbon foils obtained using EELS (points with error bars). In our calculation, we use $\epsilon_m = 1.5$ as an average of the dielectric constant of the medium surrounding the nanospheres, which reproduces the measured surface plasmon energies at the largest sizes. Even though there is large scatter in the experimental data, there is a clear trend of increasing plasma frequency as the particles get smaller. The blue line is our calculation of the surface plasmon energy shift resulting from electron spill-out. Usually, this spill-out gives a decrease in surface plasmon energy, but for Ag the screening of the d-electrons can, in some circumstances, push the surface plasmon energy into a region, where the dynamical $\mathrm{Re}[d_r(\omega_s)]$ is positive and gives a blueshift [17, 48]. It is clear that the blue line gives a reasonable account for the data except at the very smallest particles of a size 1–2 nm. In this region, we do expect effects from the finite size of the particles, introducing discrete energy levels and a gap at the Fermi level. Accounting for this as indicated by equation (7) and using the simple box estimation of R_0, $R_0 = 1.1a_0\sqrt{r_s}$, equation (8) results in the magenta line yielding an even better agreement with the measured data. We would like to stress that the only free parameter of this calculation is ϵ_m, which, however, is constrained in its value, since it has to yield the asymptotically measured plasmon energies. Furthermore, the resulting value is very close to the average of air and carbon used in the experiments as support. Additional EELS measurements taken on Ag particles on an Si_3N_4 substrate confirm this trend [20].

The good agreement between theory and experiment found for Ag particles on carbon foils is not fortuitous. We show this by analyzing other experiments in which Ag and also Au nanospheres are embedded in solid matrices. Figure 2 shows the calculated frequencies of the surface plasmons of Ag together with the experimental results by Charlé *et al* [45] for Ag spheres embedded in a solid argon matrix. We have used $\epsilon_m = 1.85$, which is very close

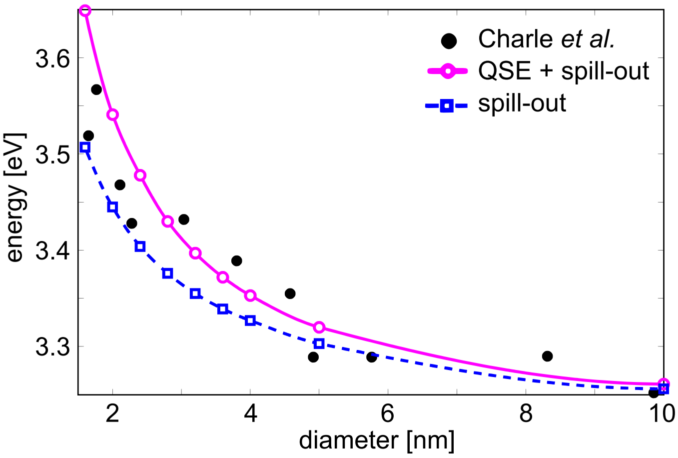

Figure 2. Surface plasmon energy shift for Ag particles embedded in a solid argon matrix. Full dots are the experimental data of Charlé *et al* [45]. The blue line shows our results from electron spill-out and the magenta line includes also the effects of size quantization.

to the value $\epsilon_m = 1.75$ quoted in [45] for solid argon. Even though ϵ_m may be considered as a fitting parameter here, one should note that the experimental spheres are not perfectly embedded in the matrix, in the sense that the matrix is not in a perfect contact with the particle surface. Therefore, values of ϵ_m different from the nominal permittivity of the matrix should be expected. The blueshift of the resonance is explained exactly on the same basis as the results of figure 1, and again this simple model is able to reproduce the experimental data on a quantitative level. Note that the maximum value of the shift measured (and calculated) is approximately 0.3 eV while it was 0.5 eV in figure 1. This is due to the fact that as ϵ_m increases, ω_s^{cl} decreases, thus moving to a region of frequencies where the dynamical $\mathrm{Re}[d_r(\omega)]$ is still positive but smaller than in the previous case.

Figure 3 shows the calculated frequencies of the surface plasmons of Ag and Au nanospheres together with the experimental results by Cottancin *et al* [9] and Lermé *et al* [18] for Ag and Au spheres embedded in alumina (black symbols). In all the calculations, we have used the value $\epsilon_m = 2.8$, which is appropriate for porous alumina [18]. As in figures 1 and 2, we show results considering only surface effects and including effects of size quantization as well.

First, we discuss the case of Ag. Note that the relevant surface plasmon energies now are pushed down below 3 eV as compared to figures 1 and 2 due to the different dielectric properties of alumina as compared to carbon/vacuum and solid argon, respectively. Here we find that surface effects cause a *redshift* of the resonance. This is because, as we have anticipated, an increased value of ϵ_m has moved the classical Mie frequency to the region of negative values of $\mathrm{Re}[d_r]$, thus changing the sign of the shift. Then for Ag we are usually in a region where the spill-out effect can go both red and blue for a small change in frequency. In this case, the effects of size quantization compensate the redshift by way of keeping the energy of the surface plasmon almost constant as the size decreases, as seen in the experiment.

In the case of Au, we also obtain that surface effects would shift the frequency toward the red but now the blueshift resulting from size quantization is stronger, producing the net blueshift shown in the figure. For Au we use an R_0, which is 40% larger than for Ag. A possible reason for this is that even though electrons in the d-bands will, in principle, also experience size effects,

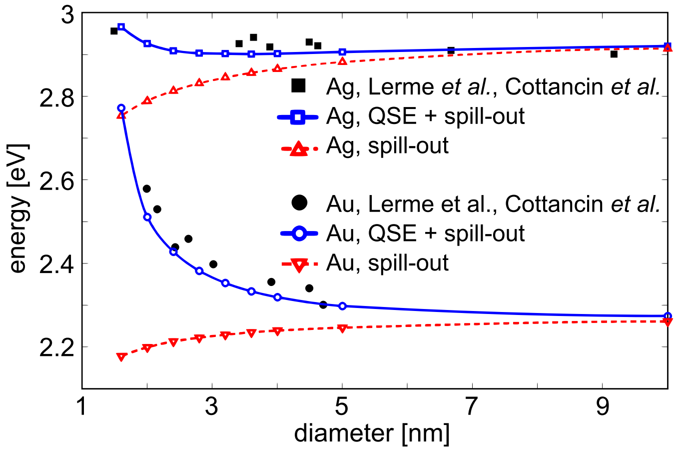

Figure 3. Surface plasmon energy positions of Ag and Au particles embedded in porous alumina. Full black symbols without a line represent the experimental data for Ag (squares) and Au (dots) from works of Lermé *et al* [18] and Cottancin *et al* [9]. The red lines represent our results from electron spill-out and the blue lines also include QSE. We see here that for Ag (top) we are in a redshifted spill-out region. However, for very small particles, the QSEs contribute a shift in the opposite way, which even upsets the redshift. In the bottom part of the figure, we illustrate that our treatment also works for other metal particles, in this case gold.

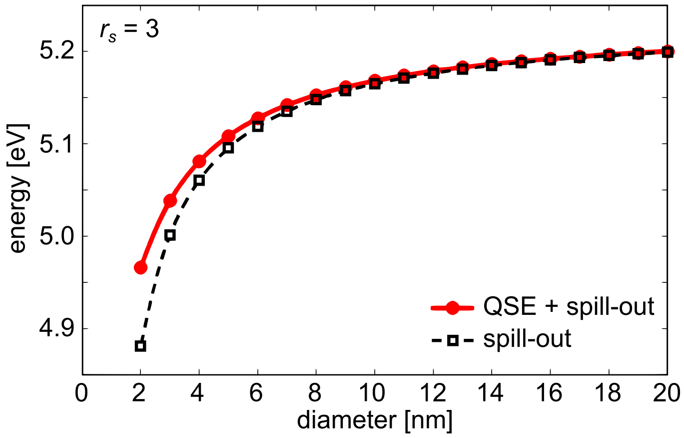

Figure 4. Surface plasmon energy positions of free-electron-metal particles of $r_s = 3$ in vacuum. The redshift produced by surface spill-out cannot be overcome by effects of size quantization as in the case of Au and Ag and the surface plasmon moves to lower energies with decreasing size.

these should be smaller for Ag with deeper d-bands than for Au. Note in equation (8) how the relative surface versus QSEs depend on $\epsilon_d(\omega)$. This effect is illustrated in the calculations we present next, for which $\epsilon_d(\omega) = 1$.

Figure 4 shows our results for free-electron metal-nanospheres of $r_s = 3$ in vacuum, using as before the simple box estimate for R_0. This is an example where the surface effects are practically responsible for the strong redshift of the surface resonance, the size quantization effects being unable to compensate for it. We would like to mention that sophisticated calculations for this system have produced redshifts of the surface resonances [1, 5]. The value we find for a radius of $R = 0.74\,\mathrm{nm}$ is $\omega_\mathrm{s} = 0.94\omega_\mathrm{s}^\mathrm{cl}$, which is close to the value $\omega_\mathrm{s} = 0.91\omega_\mathrm{s}^\mathrm{cl}$ obtained by Townsend and Bryant [5] using TDDFT. Moreover, a net redshift of these resonances has been measured for nanospheres of the typical free-electron-metals Na and K in [7] and the same behavior is expected for other such metals as Al and Mg.

We have presented a theoretical model that combines known concepts of surface dynamical screening and quantization due to size into a new formulation for the size dependence of the surface plasmon resonances in metallic nanospheres. Our results are in good agreement with existing sophisticated calculations only feasible for very small systems and yield excellent quantitative agreement with a variety of available experimental results for spheres of nanometric size. We find that the effects of the spill-out of the electronic charge at the surface of the nanoparticle, which can move the surface plasma energy toward the red or the blue depending on the material parameters of the metal and the surrounding medium, are never negligible in comparison to effects of size quantization which are also present in these small systems. We thus conclude that we would expect to unambiguously see effects of size quantization in the surface plasmon resonances of nanosystems much closer to 1 nm in size than to 10 nm, as was earlier suggested. The present investigation also points to the importance of an appropriate description of surface screening by the spill-out electrons in the case of dimers with a gap of the order of $2\mathrm{Re}\,[d_r]$ or smaller, since in this case the screening electrons can tunnel between the two particles. One should then expect the screening charge density to develop a shape strongly dependent on the model and hence influence the predicted plasmonic properties of the dimer. Finally, in this paper, we have focused on the spectral position of the surface plasmons, leaving aside the important aspect of their width. Since there are other mechanisms contributing to the width different from those discussed here in the context of the position, we will defer that study to a forthcoming publication.

Acknowledgments

We thank T López-Ríos for useful discussions. RCM acknowledges financial support from the Spanish Mineco, project FIS2011-26516. TJA and SPA acknowledge financial support from the Swedish Foundation for Strategic Research via the Functional Electromagnetic Metamaterials project SSF RMA 08.

References

[1] Ekardt W 1984 *Phys. Rev.* B **29** 1558–64
[2] Ekardt W 1984 *Phys. Rev. Lett.* **52** 1925–8
[3] Puska M J, Nieminen R M and Manninen M 1985 *Phys. Rev.* B **31** 3486–95
[4] Beck D E 1987 *Phys. Rev.* B **35** 7325–33
[5] Townsend E and Bryant G W 2012 *Nano Lett.* **12** 429–34
[6] Tiggesbäumker J, Köller L, Meiwes-Broer K H and Liebsch A 1993 *Phys. Rev.* A **48** R1749–52
[7] Reiners T, Ellert C, Schmidt M and Haberland H 1995 *Phys. Rev. Lett.* **74** 1558–61
[8] Yannouleas C 1998 *Phys. Rev.* B **58** 6748–51

[9] Cottancin E, Celep G, Lermé J, Pellarin M, Huntzinger J, Vialle J and Broyer M 2006 *Theor. Chem. Acc.* **116** 514–23

[10] Savage K J, Hawkeye M M, Esteban R, Borisov A G, Aizpurua J and Baumberg J J 2012 *Nature* **491** 574–7

[11] Teperik T V, Nordlander P, Aizpurua J and Borisov A G 2013 *Phys. Rev. Lett.* **110** 263901

[12] Ciracì C, Hill R T, Mock J J, Urzhumov Y, Fernández-Domínguez A I, Maier S A, Pendry J B, Chilkoti A and Smith D R 2012 *Science* **337** 1072–4

[13] Garcia-Etxarri A, Apell P, Käll M and Aizpurua J 2012 *Opt. Express* **20** 25201–12

[14] Smithard M 1973 *Solid State Commun.* **13** 153–6

[15] Genzel L, Martin T and Kreibig U 1975 *Z. Phys.* B **21** 339–46

[16] Ganière J D, Rechsteiner R and Smithard M A 1975 *Solid State Commun.* **16** 113–6

[17] Borensztein Y, De Andrés P, Monreal R, Lopez-Rios T and Flores F 1986 *Phys. Rev.* B **33** 2828–30

[18] Lermé J, Palpant B, Prével B, Pellarin M, Treilleux M, Vialle J L, Perez A and Broyer M 1998 *Phys. Rev. Lett.* **80** 5105–8

[19] Scholl J A, Koh A L and Dionne J A 2012 *Nature* **483** 421–7

[20] Raza S, Stenger N, Kadkhodazadeh S, Fischer S V, Kostesha N, Jauho A P, Burrows A, Wubs M and Mortensen N A 2013 *Nanophotonics* **2** 131–8

[21] Peng S, McMahon J M, Schatz G C, Gray S K and Sun Y 2010 *Proc. Natl Acad. Sci. USA* **107** 14530–4

[22] Lushnikov A A and Simonov A J 1974 *Z. Phys.* A **270** 17–24

[23] Ruppin R 1975 *Phys. Rev.* B **11** 2871–6

[24] Ascarelli P and Cini M 1976 *Solid State Commun.* **18** 385–8

[25] Ruppin R 1976 *J. Opt. Soc. Am.* **66** 449–53

[26] Boardman A D and Paranjape B V 1977 *J. Phys. F: Met. Phys.* **7** 1935–45

[27] Mie G 1908 *Ann. Phys.* **25** 377–445

[28] Feibelman P J 1982 *Prog. Surf. Sci.* **12** 287–407

[29] Apell P and Ljungbert A 1982 *Phys. Scr.* **26** 113–8

[30] Apell P and Penn D R 1983 *Phys. Rev. Lett.* **50** 1316–9

[31] Penn D R and Apell P 1983 *J. Phys. C: Solid State Phys.* **16** 5729–43

[32] Harris J and Griffin A 1971 *Phys. Lett.* A **34** 51–2

[33] Feibelman P J 1973 *Phys. Rev. Lett.* **30** 975–8

[34] Feibelman P J 1974 *Phys. Rev.* B **9** 5077–98

[35] Feibelman P J 1975 *Phys. Rev.* B **12** 1319–36

[36] Liebsch A 1985 *Phys. Rev.* B **32** 6255–60

[37] Liebsch A 1987 *Phys. Rev.* B **36** 7378–88

[38] de Andrés P, Monreal R and Flores F 1985 *Phys. Rev.* B **32** 7878–89

[39] García de Abajo F J 2010 *Rev. Mod. Phys.* **82** 209–75

[40] David C and García de Abajo F J 2011 *J. Phys. Chem.* C **112** 19470–5

[41] Raza S, Toscano G, Jauho A P, Wubs M and Mortensen N A 2011 *Phys. Rev.* B **85** 121412

[42] Fernández-Domínguez A I, Wiener A, García-Vidal F J, Maier S A and Pendry J B 2012 *Phys. Rev. Lett.* **108** 106801

[43] Penn D R 1962 *Phys. Rev.* **128** 2093–7

[44] Gorkov L P and Eliashberg G M 1965 *Sov. Phys.—JETP* **21** 940–7

[45] Charlé K P, Schulze W and Winter B 1989 *Z. Phys.* D **12** 471–5

[46] Johnson P and Christy R 1972 *Phys. Rev.* B **6** 4370–9

[47] Liebsch A 1993 *Phys. Rev. Lett.* **71** 145–8

[48] Liebsch A 1993 *Phys. Rev.* B **48** 11317–28