Electron Temperature Dependence of the Optical Properties of Small Sodium Nanoparticles

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(Dated: August 15, 2014)

We report a novel behavior of the surface plasmon linewidth in sodium nanospheres Na_{1760} changing with the electron temperature, which monotonically decreases and bears a discontinuous sudden drop at high electron temperatures. Our calculation is based on the model constructed by splitting the total Hamiltonian of all valence electrons of a metallic nanoparticle into two sub-Hamiltonians and their coupling, and obtained results can be verified by the pump-probe femtosecond spectroscopy experiments. In addition, we propose that it is the size uncertainty of small nanoparticles that yields the intrinsic linewidth of the surface plasmon resonance, which is supported by the available data of clusters Na_8 and Na_20.

PACS numbers: 73.20.mf, 31.15.xr, 36.40.Gk, 36.40.Vz

When illuminated by a light with proper frequency, the delocalized valence electrons of a metallic nanoparticle (MNP) will be excited to perform collective oscillations against ions, the so-called surface plasmon resonance (SPR). MNPs could enable strong optical absorption and scattering in deep subwavelength scale, with spectral properties determined by their composition, size, geometry, charge and surrounding medium [1]. The application based on different features of SPR flourished in many areas, such as surface-enhanced Raman scattering [2], single molecule detection [3], plasmon rulers [4]. Besides nanophotonics, SPR is also finding use in biology, catalysis, quantum optics and quantum information transfer. The capability of plasmonic systems to manipulate and enhance optical signals at nanoscale has paved the way for many novel concepts and applications, which requires a deep understanding of physics occurred in MNPs.

Based on the features of MNPs interacting with lights, different models and theories have been constructed. For large MNPs (≥ 100 nm), the quantum effect is negligible and their optical properties can be well described by classical Drude dielectric function \( \epsilon(\omega) = 1 - \omega_p^2/\omega(\omega + i\gamma) \), where \( \omega_p = (4\pi\rho_e e^2/m)^{1/2} \) is the Mie frequency of the plasmon resonance, \( \gamma^{-1} \) the relaxation time, and \( e \), \( m \) and \( \rho_e \) the electron charge, mass and density respectively. Classical plasmonics systems yield resonance at Mie frequency which does not depend on MNPs’ size. For quantum plasmonic systems, the time-dependent local density approximation (TDLDA) and all kinds of random phase approximation methods (RPA) are powerful tools to study their optical properties [5,6,7]. For medium-sized MNPs with radii 10 – 60 nm, their optical properties are quite difficult to accurately describe as the situations of very small and very large MNPs. Many non-fundamental methods were also developed for the optical properties of MNPs with sizes from several nanometers to several tens of nanometers [8,9,10]. For MNPs smaller than 5 nm, the model constructed by separating the coordinates of all delocalized valence electrons into the coordinate of the center of mass and relative coordinates describes the SPR as the oscillation of the center-of-mass, and the SPR is damped by the coupling between the center of mass of valence electrons and electrons outside the nanoparticle (SCRM) [11,12].

Although the SCRM is fundamental and elegant, the results done previously are not satisfactory. As a matter of fact, the best founded TDLDA and all kinds of RPA methods are not perfect either. It is believed that the full linewidth of the SPR comprises an intrinsic part \( \gamma_i \) and a size-dependent part \( \gamma_s(a) \). However, neither TDLDA nor RPA methods touch upon the calculation of the intrinsic linewidth, and its generation mechanism is still an open question. For bulk metals, the intrinsic linewidth of the SPR is caused by the scattering of delocalized electrons by phonons, impurities and defects. For small MNPs, electron states are quantized into discrete levels due to strong quantum confinement effect and the scattering of a delocalized electron experienced in bulk metals does not exist, which foreshadows a different generation mechanism for the intrinsic linewidth of small MNPs. In this letter, we will use SCRM to study the optical properties of nanospheres Na_{1760} in detail and explore the generation mechanism of the intrinsic linewidth.

For alkali metals, the optical properties is mainly determined by delocalized valence electrons, and ionic cores can be treated as a uniform background. For nanoparticles with valence electrons closing angular momentum shells, such as Na_{1760}, their shapes can be thought of as perfect spheres. For such a sodium nanoparticle composed of \( N \) atoms in vacuum, by introducing the coordinate of the center of mass \( \mathbf{R} = (\sum \mathbf{r}_i)/N \) and its conjugate momentum \( \mathbf{P} = \sum \mathbf{p}_i \), the total Hamiltonian \( \mathcal{H} \) of all delocalized valence electrons denoted by coordinate and momentum pairs \( (\mathbf{r}_i, \mathbf{p}_i) \) can be separated into three parts \( \mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{12} \), and the detailed derivation
can be found in the supplementary information. Three terms of total Hamiltonian $\mathcal{H}$ are

$$\mathcal{H}_1 = \frac{\mathbf{P}^2}{2Nm} + \frac{1}{2}N\sum_{\alpha}q^2 \mathbf{R}^2$$

$$\mathcal{H}_2 = \sum_{i=1}^{N} \left( \frac{\mathbf{\hat{r}}_i^2}{2m} + U(\xi_i) \right) + \frac{\hbar^2}{8\pi^2\varepsilon_0} \sum_{i \neq j} \frac{1}{|\xi_i - \xi_j|}$$

$$\mathcal{H}_{12} = \frac{Ne^2}{4\pi\varepsilon_0a^3} \mathbf{R} \cdot \sum_{i=1}^{N} \xi_i \left( \alpha^2 - 1 \right) \Theta(\xi_i - a)$$

(1)

respectively, where $\xi_i = |\xi_i|$; $a$ and $\Theta(x)$ are the radius of nanospheres and the Heaviside step function; $\xi_i = \mathbf{r}_i - \mathbf{R}$ and $\mathbf{\hat{r}}_i = \mathbf{\hat{r}}_i - \mathbf{P}/N$ are the relative coordinate and relative momentum of the $i$-th electron. The single electron confining potential $U(|\xi| + \mathbf{R})$ produced by ionic background was expanded to the second order at $|\mathbf{R}| = 0$. The Hamiltonian $\mathcal{H}_1$ has the harmonic oscillator structure of the center of mass, where $N_{out} = \sum_i \Theta(\xi_i - a)$ is the number of spill-out electrons. The quanta of the Hamiltonian $\mathcal{H}_1$ correspond to SPR excitations in MNPs. The Hamiltonian $\mathcal{H}_2$ describes the degree of freedom of relative coordinates of all valence electrons. The third part $\mathcal{H}_{12}$ shows that the SPR couples not to electrons inside the nanosphere but to those outside the nanosphere.

The Hamiltonian $\mathcal{H}_1$ can be further expressed as $\mathcal{H}_1 = \sum (n + 1/2)h\Omega p \hat{b} \hat{b}^\dagger$, and the annihilation operator $\hat{b}$ is defined as

$$\hat{b} = \frac{\sqrt{Nm\Omega_p}}{2\hbar} \mathbf{R} + \frac{i}{\sqrt{2N\hbar m\Omega_p}} \mathbf{P},$$

(2)

where $i$ is the imaginary unit. The potential energy part of $\mathcal{H}_2$ is usually approximated by a mean field which transforms the many body problem into a single particle problem, so the $\mathcal{H}_2$ can be expressed as $\mathcal{H}_2 = \sum_\alpha \epsilon_\alpha \hat{c}^\dagger_\alpha \hat{c}_\alpha$. The energy levels and corresponding wavefunctions of $\mathcal{H}_2$ can be obtained by solving the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\xi)\right)\psi_\alpha(\xi) = \epsilon_\alpha \psi_\alpha(\xi),$$

(3)

where the single particle effective potential $V_{eff}$ can be obtained by LDA calculation [11]. Because a systematic multi-step approximation method has been developed by the authors to solve Schrödinger equation with a Woods-Saxon-like potential [14], total 134 energy levels and corresponding piecewise analytical wavefunctions with high accuracy are obtained for nanospheres Na1760, which makes it possible to accurately calculate the optical properties of Na1760.

The coupling $\mathcal{H}_{12}$ can be recast as

$$\mathcal{H}_{12} = A(\hat{b} \hat{b}^\dagger + \hat{b} \hat{b}) \sum_{\alpha, \beta} d_{\alpha, \beta} \hat{c}^\dagger_\alpha \hat{c}_\beta ,$$

(4)

where $\epsilon_\alpha = \epsilon_\alpha - \epsilon_\beta$, and $f(\epsilon) = 1/(1 + e^{(\epsilon - \mu)/k_B T})$ is the Fermi-Dirac distribution; $\mu$ the electron temperature, the Boltzmann constant and the chemical potential respectively. The values of $\mathcal{A}$ and $\Omega_p$ are determined by the radius $a = N^{1/3}\rho_s$, and $\rho_s$ is the Wigner-Seitz radius. However, the value of $\rho_s$ for sodium nanoparticles appeared in references varies from 3.93a_0 to 4.3a_0 being quite dispersive [8, 9, 11, 12], where $a_0 = 0.529$ A is the Bohr radius. We calculated the energy of the SPR of Na1760 changing with $\hbar\omega_p$ and results are shown in Fig. 1. Only within a very narrow range of $\hbar\omega_p$ does the coupling $\mathcal{H}_{12}$ yields the frequency redshift of the SPR. The SPR energy $h\Omega_q = 3.324$eV of the TDLDA calculation just locates in this redshift range [11], which corresponds to the radius $a = 25.313$ A and $\rho_s = 3.962a_0$. The cusps in Fig. 1 correspond to the situation that the Eq. (3) is invalid due to the approximate degeneracy between the SPR state and electron-hole states.

The evolution of the SPR energy of Na1760 with different charges with the electron temperature is presented in Fig. 2 which first shows a redshift trend from zero temperature up to $T \sim 400$ K and then presents an explicit blueshift behavior. This evolution pattern is the same as

![FIG. 1: The SPR energy $h\Omega_q$ (dotted line) calculated according to Eq. (5) and $h\Omega_p$ (red line) for Na1760 versus the classical plasmon energy $h\omega_p$. The divergent values corresponding to $\epsilon_{\alpha, \beta} \sim \Omega_p$ have been properly minimized for the sake of display.](image-url)
Therefore, a reasonable choice of $2\delta\epsilon$ is the smallest average value of two energy widths of particle-hole pairs satisfying Eq. (8), namely $2\delta\epsilon = \min\{\sqrt{4\epsilon_\alpha\epsilon_\alpha} + \sqrt{4\epsilon_\beta\epsilon_\beta}\}$. Thus, it is shown that the SPR linewidth has not been reported before, which is quite different from our results.

FIG. 2: The SPR energy of nanospheres $\text{Na}_{1760}$ with different charges as a function of the electron temperature. The lowest line is for the situation of $q = -4|\epsilon|$, and $e$ is the charge of an electron.

those of $\text{Na}_{138}$ and $\text{Na}_{139}^{+}$ [10]. However, it is astonishing that the turning temperature (1000K for $\text{Na}_{138}$ and 2500K for $\text{Na}_{139}^{+}$) drastically changes with the charge of nanospheres, which is quite different from our results.

The linewidth is another significant quantity to characterize the optical properties of MNPs. The size-dependent linewidth of the SPR in small MNPs is determined by Landau damping mechanism and can be expressed as

$$h\gamma_s(a) = B \sum_{\alpha\beta}[1 - f(\epsilon_\alpha)]f(\epsilon_\beta)|d_{\alpha\beta}|^2(\epsilon_\alpha - h\Omega_p), \quad (6)$$

where $B = \frac{\hbar^4N^2}{16\pi m_c^2\delta}\gamma_s(a)$, and Dirac function $\delta(\epsilon_\alpha - h\Omega_p)$ represents the condition of energy conservation. However, there are no particle-hole pairs of $\text{Na}_{139}$, which is quite different from our results. Weick et al. obtained the opposite result that the SPR linewidth of $\text{Na}_{1760}$ monotonically increases with the electron temperature [11]. Hervieux and Bigot also obtained the result that the SPR linewidths of $\text{Na}_{138}$ and $\text{Na}_{139}$ increase with the electron temperature [16]. We notice that although the temperature effect is included, the SPR linewidth of $\text{Na}_{138}$ calculated by Hervieux and Bigot is quite smaller than that of matrix RPA calculations [15]. Our calculated result, the SPR size-dependent linewidth (0.224eV) at the zero electron temperature, is the same as that of TDLDA calculation [11]. This novel behavior of SPR linewidth of $\text{Na}_{1760}$ can be easily understood.

FIG. 3: The size-dependent linewidth $h\gamma_s(a)$ of nanoparticles $\text{Na}_{1760}$ with different charges as a function of the electron temperature.

SPR in $\text{Na}_{1760}$ with different charges, which monotonically decreases with the increasing electron temperature and bears a discontinuous sudden drop at high electron temperatures. To our knowledge, this novel behavior of the SPR linewidth has not been reported before, which is completely different from those obtained by other authors. Weick et al. obtained the opposite result that the SPR linewidth of $\text{Na}_{1760}$ monotonically increases with the electron temperature [11]. Hervieux and Bigot also obtained the result that the SPR linewidths of $\text{Na}_{138}$ and $\text{Na}_{139}$ increase with the electron temperature [16]. We notice that although the temperature effect is included, the SPR linewidth of $\text{Na}_{138}$ calculated by Hervieux and Bigot is quite smaller than that of matrix RPA calculations [15]. Our calculated result, the SPR size-dependent linewidth (0.224eV) at the zero electron temperature, is the same as that of TDLDA calculation [11]. This novel behavior of SPR linewidth of $\text{Na}_{1760}$ can be easily understood. When the electron temperature increases, valence electrons have larger possibility to occupy the higher energy levels leading to the smooth decrease of $\gamma_s(a)$. At the same time, valence electrons have larger possibility to stay outside leading to the slight decrease of the frequency $\Omega_p$, which in turn alters the number of particle-hole pairs involved in the SPR damping yielding the sudden drop of the linewidth. The sudden drop in Fig. 3 is caused by the number of particle-hole pairs decreasing from 29 to 28. In the following we will show that this novel behavior of the SPR linewidth of $\text{Na}_{1760}$ would be slightly enhanced by its intrinsic linewidth and could be verified by the pumpprobe femtosecond spectroscopy experiments.

The studies on the intrinsic linewidth of the SPR are precious few. It is believed that the coupling of the dipole SPR to the quadrupole shape fluctuations of positive ions produces the intrinsic linewidth proportional to $(T/N)^{1/2}$ [19]. However, this thermal mechanism of the intrinsic linewidth is questionable, which would lead to the corollary that the intrinsic linewidth vanishes when the ions temperature decreases to zero. Furthermore, the
The intrinsic linewidth would not weaken the novel behavior of the size-dependent linewidth of Na_{1760}, and we expect that this novel behavior could be verified in future by the elaborate pump-probe femtosecond spectroscopy experiments.

This work was supported by the NSF of People’s Republic of China under contract No.10904115.

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