A Confined Electron Spherical Void Model in Sonoluminescence

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A confined electron spherical void model generalized from the rectangular box one is used for the discussion of the radical spectrum emitted from nonhomogeneous hot dense helium gas in sonoluminescence. The theoretical analysis shows that the gas can emit a continuous spectrum from 3s to 2p that fits with the experimental data in the visible window of single-bubble sonoluminescence.

The confined electron model of an atom was used for the interpretation of the mechanism of the continuous spectrum for single-bubble sonoluminescence (SBSL).[1] The model assumes that electrons are confined in a rectangular box with variable size and discusses the transition radiation. For a certain void size, the particle-in-a-void model predicts discrete emission lines. Blurring of these emission lines, due to the distribution of void dimensions, produces a continuous spectrum. Gas in a collapse bubble is in a nonhomogeneous hot dense state in SBSL.[2] Two important facts are clarified in ref 1 one is that the distribution of the dimension of the confined electron voids can make the discrete emission spectrum continuous, the other is that the continuous spectrum depends on two parameters at least for a certain nonhomogeneous system, which is apparent in the means of thermodynamics. The equilibrium thermal emission spectrum depends only on one parameter, the temperature T. To describe the nonhomogeneous state, we need another parameter. As we know, the distribution of the electrons in an atom is close to a spherical shape, which is more natural and compendious than a rectangular box, so a spherical void model is generalized from the rectangular one. In this letter, we will use the method of Michels et al.[3] for the transition radiation of helium gas in SBSL, assuming electrons are confined in a spherical void with the radius r_0. With the postulate of the most probable distribution, the radius r_0 has a Gaussian distribution. The theoretical spectrum of the transition from 3s to 2p fits the experimental data in the visible window of SBSL[2,4] smoothly.

First, we consider the homogeneous hot dense gas of helium. If the electrons are confined in a spherical void with a radius r_0, the wave function of helium molecule can be written as

$$\Psi = \psi_1\psi_2 \tag{1}$$

where ψ_1 and ψ_2 are the wave functions of the two electrons, respectively. Moreover, ψ_1 and ψ_2 can be approximately treated as the wave functions of the hydrogen atom satisfying the equation

$$i\hbar\frac{\partial\psi_j}{\partial t} = \hat{H}(t)\psi_j \qquad j = 1,2 \tag{2}$$

where $\hat{H}(t) = \hat{H}_0 + \hat{H}(t)$ ($\hat{H}'(t)$ is the part of time-dependent perturbation). For $\hat{H}'(t) = 0$, we have $\psi = \sum_n a_n\phi_n$, $\phi_n = \varphi_n e^{-i/hE_n t}$, φ_n is proper function of the time-independent part $\hat{H}_0$. The equation of the radial part of ϕ_n can be written as follows (in atomic units)

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[2E + \frac{2}{r} - \frac{l(l+1)}{r^2}\right]R = 0 \tag{3}$$

where E is the total energy and l is the angular quantum number. In this model, the wave function must have a zero point at $r = r_0$.

Defining $\rho = 2r/n$ and $E = -1/(2n^2)$, we can obtain the radial part of the wave function as

$$R = e^{-(1/2)\rho}\rho^l F(l+1-n,2l+2,\rho) \tag{4}$$

where $F(l+1-n,2l+2,\rho)$ is a confluent hypergeometric function. The boundary condition here is $R(r_0) = e^{-(1/2)\rho_{0\rho_0^l}}F(\rho_0) = 0$. It is difficult to find an analytical expression of the confluent hypergeometric function, so we will discuss the numerical solution based on dividing the total energy into different regions. Some approximate steps are needed to get the numerical solution here.

When $E < 0$ and r_0 is infinite, n is equal to the main quantum number. If r_0 is not infinite but still large enough that n is nearly the main quantum number, we can write $n = N + \beta$, where N is the main quantum number, and β is the retouch. When the hydrogen atom is free, n is equal to the main quantum number N, and the boundary condition gives a polynomial. For the nonzero β, the boundary condition gives an infinite series, which can be used for find β.[3] The equations of β for 2p and 3s are

$$\beta_{2p} = \frac{1}{6\sum_{\sigma=1}^{\infty}\frac{1}{\sigma(\sigma+3)!}r_0^{\sigma}} \tag{5}$$

$$\beta_{3s} = \frac{1 - \frac{2}{3}r_0 + \frac{2}{27}r_0^2}{2\sum_{\sigma=3}^{\infty}\frac{1}{\sigma(\sigma-1)(\sigma-2)(\sigma+1)!}(^2/_3 r_0)^{\sigma} + \frac{1}{9}r_0 - \frac{5}{81}r_0^2} \tag{6}$$

When n is an integer, the confluent hypergeometric function degenerates into a derivative of a Laguerre polynomial

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$$F(l+1-n,2l+2,\rho) = \frac{(n-l-1)!}{(2l+2)_{n-l-1}} L_{n-l-1}^{2l+1}(\rho) \qquad (7)$$

where

$$(2l+2)_{n-l-1} = (2l+2)(2l+3)\ldots[(2l+2)+(n-l-1)-1]$$

For the rest part of this region, we can use interpolation procedure to find the numerical solution.

When n is infinite, the total energy is zero. In this case, the confluent hypergeometric function can be simplified as a Bessel function as follows

$$\lim_{n\to\infty} F(l+1-n,2l+2,\rho) \to J_{2l+1}(2\sqrt{n\rho}) = J_{2l+1}(2\sqrt{2r}) \qquad (8)$$

The nodes of the Bessel function correspond to the points where the total energy is zero, and the radii related are $r_{02p}^* = 5.08831$ and $r_{03s}^* = 12.9374$, respectively.

When $E > 0$, the number n is a pure imaginary. The confluent hypergeometric function degenerates into an M function[5]

$$F(l+1-n,2l+2,\rho) = \rho^{-(l+1)} e^{\rho/2} M_{n,(2l+1)/2}(\rho) \qquad (9)$$

where

$$M_{\gamma,p/2}(\rho) = \frac{\Gamma(p+1)}{2^{\gamma}\Gamma\left(\frac{p+1}{2}+\gamma\right)\Gamma\left(\frac{p+1}{2}-\gamma\right)} \rho^{(p+1)/2} \int_{-1}^{1} (1-t^2)^{(p-1)/2} \left(\frac{1-t}{1+t}\right)^{\gamma} e^{(\rho/2)t}\, dt \qquad (10)$$

When $E \to \infty$, we can set n approach to zero in the eq 3 and $\rho = 2rn^{-1} = 2ir\sqrt{2E}$. Then the radial part of ϕ_n is the *Bessel* function as

$$R = J_{l+(1/2)}(r\sqrt{2E}) \qquad (11)$$

and we can educe the functions of asymptote as follows

$$E_{2p} = \frac{(4.49341)^2}{2r_0^{\,2}} \qquad (12)$$

$$E_{3s} = \frac{9\pi^2}{2r_0^{\,2}} \qquad (13)$$

From these equations, $E^{-1/2} = E^{-1/2}(r_0)$ are straight lines through the origin, and these lines are tangents to $(E^{-1/2}, r_0)$ curves at zero point. At the same time, $r_0 = r_0^*$ is an asymptote of the $(E^{-1/2}, r_0)$ curve. Therefore, we can define as $E^{-1/2} = 2r_0^* k/\pi \tan(r_0\pi/2r_0^*)$, where k is the tangential slope. As above stated, we can give the whole (E, r_0) curve as shown in Figure 1.

In atomic units, the transition probability is $w \propto |r_{21}|^2$, and the transition frequency is $\upsilon_{21} = E_2 - E_1$, where $r_{21} = \int_0^{r_0} R_1^* r R_2 r^2\, dr$, $R_1(r)$ and $R_2(r)$ are normalized radial wave functions of initial and final states for the transition, respectively. One energy unit corresponds to the energy of a photon whose wavelength is 45.588 nm in this unit. Therefore, we may give the relation (w, r_0) and (υ, r_0) for the transition between 2p and 3s, because the transitions between the two lower excited energy levels is required to describe the emission spectrum within the 200−700 nm wavelength region covered by the SBSL experiments.

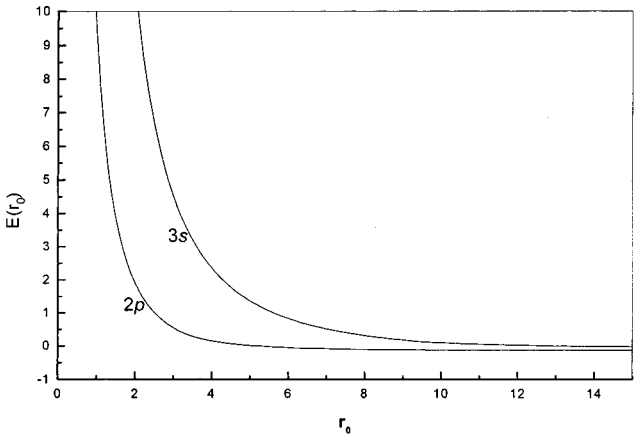

Figure 1. (E, r_0) curves of the 2p and 3s energy levels in atomic units.

A nonhomogeneous hot dense gas in a bubble can be regarded as an assembly of many molecular clusters. Each cluster can come to a homogeneous equilibrium state quickly if the gas molecules collide sharply, and it has a certain pressure and temperature. Moreover, there is a continuous distribution for pressure and density in the bubble due to the nonhomogeneous character of the gas. It means that the pressure and the temperature are different in different clusters. For the model of electrons confined in a spherical void with the radius r_0,[3] the kinetic energy of electrons and nuclei of each cluster in the bubble is given by

$$\bar{T} = -r_0 \frac{\partial E}{\partial r_0} - E \qquad (14)$$

where E is the total energy. The virial theorem for the gas of pressure P and volume V gives

$$\Delta\bar{T} = 3\Delta(PV) - \Delta E \qquad (15)$$

Above equations show that the pressure P of a cluster determines the average spherical radius r_0. In the cluster, the continuous distribution for pressure in the bubble will make the radius r_0 has a continuous distribution too, as a result the spectrum will become continuous.

Let a is the mean radius of spherical voids in the bubble. If the distribution of the radius r_0 is $f(r_0 - a)$, it must satisfy the following relations

$$\int_{-a}^{\infty} f(r_0-a)d(r_0-a) = 1 \qquad (16)$$

and

$$\int_{-a}^{\infty} (r_0-a)^2 f(r_0-a)d(r_0-a) = \sigma \qquad (17)$$

where σ is a parameter to be confirmed. Therefore, the most probable distribution of $f(r_0 - a)$ is approximately a Gaussian one

$$f(r_0) = A\frac{1}{\sqrt{2\pi\sigma}} e^{-(r_0-a)^2/2\sigma} \qquad (18)$$

where A is a normalization constant. This means that there exist two free parameters in the description, which is similar to the $D(a)$ in the rectangular model.[1] The light intensity due to transition is given by $I(r_0) = Bf(r_0)\, w(r_0)\, \upsilon(r_0)$, where the coefficient B includes the effect of the initial gas atom number and the ionization efficiency. Therefore, the relationship between

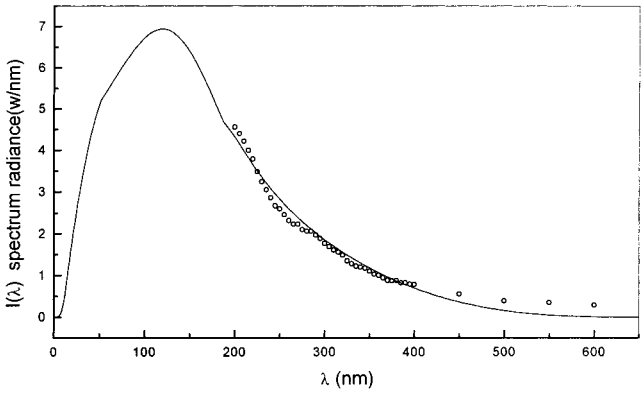

Figure 2. (I, λ) curve of the transition from 3s to 2p, and the cycles represent the experimental data of the bubble filling with helium in water.

light intensity and wavelength may be described as the curve shown in Figure 2, where $a = 1.54$ Å and $\sigma = 8.2$ Å^2.

In the Figure 2, the cycles represent the experimental data of the bubble filling with helium in water.[3,4] The figure shows that the theoretical spectrum of the transition from 3s to 2p fits with the experimental data in the visible window of SBSL smoothly.

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