Application of density-functional theory to line broadening: Cs atoms in liquid helium

Takashi Nakatsukasa
Physics Department, Tohoku University, Sendai 980-8578, Japan

Kazuhiro Yabana
Institute of Physics, University of Tsukuba, Tennodai 1-1-1, Tsukuba 305-8571, Japan

George F. Bertsch
Physics Department and Institute for Nuclear Theory, University of Washington, Seattle, Washington 98195
(Received 10 October 2001; published 22 February 2002)

We test the applicability of density-functional theory (DFT) to spectral perturbations taking an example of a Cs atom surrounded by superfluid helium. The atomic DFT of helium is used to obtain the distribution of helium atoms around the impurity atom, and the electronic DFT is applied to the excitations of the atom, averaging over the ensemble of helium configurations. The shift and broadening of the $D_1$ and $D_2$ absorption lines are quite well reproduced by theory, suggesting that the DFT may be useful for describing spectral perturbations in more complex environments.

DOI: 10.1103/PhysRevA.65.032512 PACS number(s): 32.70.Jz, 67.40.Yv, 71.15.Mb

I. INTRODUCTION

The time-dependent density-functional theory (TDDFT) has proved to be a powerful tool in the description of optical absorption for molecules and clusters in free space (for a review, see Ref. [1]; more recent citations can be found in Refs. [2,3]). We would like to know whether the theory can be extended to calculate the line shifts and broadening when the absorber is embedded in a medium. Most applications have treated electronic excitations from a single frozen nuclear configuration representing the ground state of an isolated molecule or an ideal crystal, in which case the predicted absorption lines are sharp below the photoionization threshold. Recently it was shown that the TDDFT also works well in describing the broadening of the transitions and the strength of symmetry-forbidden transitions due to zero-point vibrational motion, taking the example of the benzene spectrum [4]. In the present work, we will calculate the effects of external perturbations on optical absorption. We choose as a simple test case a cesium atom immersed in liquid helium at low temperature, because of the simplicity both of the electronic structure and of the external perturbation. In the long term we are interested in extending this kind of analysis to more complex systems which would require the full power of the time-dependent density-functional theory.

Aside from our motivation from the perspective of applications of DFT, spectroscopic measurements of impurity atoms and molecules in superfluid helium have been attracting considerable interest in recent years [5]. The repulsive force between an impurity and helium atoms induces a bubble around the impurity. This leads to a weak perturbation by the helium atoms on the spectra of impurities. The line shifts and spectral shapes induced by the helium perturbation provide information on the properties of the bubble in the quantum liquid as well as the excited states of the impurity. Since the perturbation is weak, this method also provides a unique tool for spectroscopic measurements of atomic clusters at low temperature [6–8].

Perturbations of cesium lines have been studied experimentally as a function of helium pressure [9] and we shall calculate this system. There are two $s$-$to$-$p$ transitions, the $D_1$ ($s_{1/2} \rightarrow p_{1/2}$) and $D_2$ ($s_{1/2} \rightarrow p_{3/2}$) lines, both of which are blueshifted and acquire widths in a helium bath. The shifts and widths of the two lines are different, and the $D_2$ line has a skewed shape suggesting a double-peak structure. These features were first analyzed with a collective vibration model of the helium bubble [10]. That model reproduced average peak shifts, but gave linewidths less than one-half of observed ones. A more sophisticated analysis has been made treating the liquid helium environment by the path-integral Monte Carlo method [11]. This quantum simulation successfully reproduced observed $D_2$ line profiles of the Cs spectrum. However, the method is very costly in computer resources. We are thus motivated to develop an approach to treating helium perturbation that is both simple and yet has quantitative accuracy. We will show that a density-functional theory together with a statistical description of helium configurations meets our purpose. The helium density distribution around an embedded atom is calculated with the DFT, and the helium configurations are generated by a random sampling using the density distribution as the sampling weight function.

In addition to reporting the calculations on the absorption spectrum of cesium in helium, we offer some simple qualitative interpretation of how the qualitative features of the spectrum reflect the properties of the helium bubble around the atom.

II. FORMALISM

A. Description of liquid helium around an impurity atom

Among a number of density-functional methods for liquid helium, we adopt the Orsay-Paris functional of Ref. [12].
Although the Orsay-Paris functional is known to have some problems with the dynamical properties of liquid helium [13], it has correct long-range behavior and reasonable short-range characteristics. Since we are interested in a density profile of liquid helium, it should be adequate for our purposes.

The energy in the DFT is assumed to have the form

$$E = \int dr \mathcal{H}_0(r),$$

where

$$\mathcal{H}_0(r) = \frac{1}{2m} \left[ \nabla \sqrt{\rho(r)} \right]^2 + \frac{1}{2} \int d\mathbf{r}' \rho(r') V_{\text{LJ}}(|\mathbf{r} - \mathbf{r}'|) \rho(r') + \frac{c}{2} \rho(r)(\bar{\rho}_r)^{1+\gamma}.$$  

(2.2)

Here, $m$ is the mass of a helium atom and $\bar{\rho}_r$ is a coarse-grained density defined by

$$\bar{\rho}_r = \frac{3}{4 \pi h^3} \int_{r<h} dr \rho(r).$$  

(2.3)

The $V_{\text{LJ}}$ is a standard Lennard-Jones potential describing the He-He interaction screened at distances shorter than the distance $h$,

$$V_{\text{LJ}}(|\mathbf{r} - \mathbf{r}'|) = \begin{cases} 
4 \epsilon \left[ \alpha \left( \frac{\mathbf{r}' - \mathbf{r}}{|\mathbf{r}' - \mathbf{r}|} \right)^{12} - \left( \frac{\alpha}{|\mathbf{r}' - \mathbf{r}|} \right)^6 \right] & \text{for } |\mathbf{r} - \mathbf{r}'| \geq h \\
V_{\text{LJ}}(h) \left( \frac{|\mathbf{r} - \mathbf{r}'|}{h} \right)^4 & \text{for } |\mathbf{r} - \mathbf{r}'| < h.
\end{cases}$$

(2.4)

The values of the parameters in Eqs. (2.2), (2.3), and (2.4) are $c = 1.045 \times 10^6$ K Å$^{-3} + \gamma$, $\gamma = 2.8$, $\epsilon = 10.22$ K, $\alpha = 2.556$ Å, and $h = 2.377$ Å. This is the same density functional that was used to study atomic impurities in liquid helium [14] and sodium dimers on the surface of liquid helium [15]. In those studies, the effect of the impurity was treated by including in Eq. (2.2) a potential interaction $V_I(r)$ between the helium atoms and the impurity,

$$\mathcal{H}(r) = \mathcal{H}_0(r) + V_I(r) \rho(r).$$

(2.5)

where $\mathbf{r}_e$ and $\mathbf{r}$ are the coordinates of the electron and helium atom, respectively. The strength $V_0$ is determined from the electron-helium scattering length $a$ as

$$V_0 = \frac{2 \pi a}{m_e},$$

(2.7)

where $m_e$ is the electron mass. Then $V_I(r)$ is given by

$$V_I(r) = V_0 \rho_e(r),$$

(2.8)

where $\rho_e(r)$ is the electron density of the impurity atom. We take $a = 0.69$ Å, corresponding to the observed low-energy electron-helium cross section $\sigma = 6.0$ Å$^2$ [16]. We have also assumed that the ion core is heavy enough to be treated as a classical particle at the origin. Since Eq. (2.6) expresses the interaction between He atoms and electrons, the same interaction will be used to estimate the energy shift of valence electrons due to the helium perturbation. This treatment of the interatomic potential ignores long-range attraction due to the polarization effects. The influence of the polarization effect will be mentioned later.

Utilizing the energy functional $E[\rho] = \int dr \mathcal{H}(r)$, we calculate the density profile of liquid helium, putting the impurity atom at the origin. Minimizing the grand potential at zero temperature, $\Omega = E[\rho(r)] - \mu N$, leads to a Hartree-type equation

$$\left[ -\frac{1}{2m} \nabla^2 + U(\mathbf{r}) + V_I(\mathbf{r}) \right] \sqrt{\rho(\mathbf{r})} = \mu \sqrt{\rho(\mathbf{r})},$$

(2.9)

where

$$U(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') V_{\text{LJ}}(|\mathbf{r} - \mathbf{r}'|) + \frac{c}{2} \rho(\bar{\rho}_r)^{1+\gamma} + \frac{c}{2} (1+\gamma) \frac{3}{4 \pi h^3} \int_{|\mathbf{r} - \mathbf{r}'| < h} d\mathbf{r}' \rho(\mathbf{r}')(\bar{\rho}_r)^\gamma.$$  

(2.10)

The equation is solved with the boundary condition that the density go to the bulk density $\rho_0$ at large $r$. This is satisfied by setting the chemical potential to

$$\mu = b \rho_0 + \left( 1 + \frac{\gamma}{2} \right) c \rho_0^{\gamma+1},$$

(2.11)

where $b = \int d\mathbf{r} V_{\text{LJ}}(\mathbf{r}) = -8.8881 \times 10^2$ K Å$^3$. The bulk density is related to the pressure $P$ by

$$P = -\frac{\partial E}{\partial V} = \frac{1}{2} b \rho_0^2 \frac{\gamma + 1}{2} c \rho_0^{\gamma+2}.$$  

(2.12)

Carrying out the solution of Eq. (2.9) we find the density profile shown in Fig. 1. The three curves give $\rho(r)$ at equilibrium densities $\rho_0$ of 0.0218, 0.0239, and 0.0253 Å$^{-3}$, corresponding to $P = 0$, 10, and 20 atm, respectively. One can see a sharp rise in the density at $r = 6$ Å. This corresponds to the bubble radius. An oscillatory structure appears in the
Here $d$ is the range of a short-range correlation. The distribution function $g(r)$ is determined by the condition that the distribution of Eq. (2.14) gives a helium density $\rho(r)$,

$$\rho(r) = N \int_V d\mathbf{r}_2 \cdots d\mathbf{r}_N w_c(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N).$$  

(2.15)
We use first-order perturbation theory to evaluate the orbital shifts in the ensemble of helium configurations \( \tau = (r_1, \ldots, r_N) \). The same helium configuration is used for the ground state \( s_{1/2} \) and excited states \( p_{1/2} \) and \( p_{3/2} \), following the Frank-Condon principle. For \( s_{1/2} \) and \( p_{1/2} \) states, the energy shifts of the valence electron are then calculated as

\[
\Delta E^{(k)}(\tau) = \left( \psi^k \right) \sum_i V_{e-He}(i) \psi^k(i) = \sum_i V_0 |\psi^k(r_i)|^2,
\]

(2.16)

where \( k \) stands for orbital quantum numbers \((lj)\) and either \( m \) state may be taken. For \( p_{3/2} \) states, the matrix elements depend on \( m \) and we have to diagonalize a \( 4 \times 4 \) matrix to get the energy shifts. We then obtain two eigenenergies, each of which is doubly degenerate.

Each helium configuration produces an energy shift and possible splitting but the transitions remain sharp. The line broadening comes from the ensemble average over helium configurations. The line shape of the \( D_1 \) \((s_{1/2} \rightarrow p_{1/2})\) transition is given by

\[
S_{D_1}(E) = \int \psi^k(\tau) \delta(E - \Delta E^{(p_{1/2})}(\tau) - \Delta E^{(s_{1/2})}(\tau)) \rho_e^{(k)}(\tau) d\tau,
\]

(2.17)

where \( E \) is the shift from the energy position of the free atom. For the \( D_2 \) \((s_{1/2} \rightarrow p_{3/2})\) transition, we need to add the two eigenmodes

\[
S_{D_2}(E) = \int \psi^k(\tau) \delta(E - \Delta E^{(p_{3/2})}(\tau) - \Delta E^{(s_{1/2})}(\tau)) \rho_e^{(k)}(\tau) d\tau,
\]

(2.18)

C. Origin of peak shifts, broadening, and splitting

In this section, we discuss qualitatively how the blue-shifts, the broadening of the lines, and the splitting of \( D_2 \) transitions occur. First consider a valence electron of the alkali-metal atom interacting with a single helium atom at a position \( R \) with respect to the impurity atom. The energy shift of the valence electron is determined by the electron wave function at the position of the helium atom, \( \psi(r_e = R) \).

For \( s_{1/2} \) and \( p_{1/2} \) states, the energy shift \( \Delta e \) is calculated as

\[
\Delta e^{(k)} = V_0 \rho_e^{(k)}(R),
\]

(2.19)

as a first-order perturbation by \( V_{e-He} \). Since \( V_0 \) is positive, the energy shift in Eq. (2.19) is also positive. As may be seen from Fig. 2, the wave function of the \( p_{1/2} \) state is consideredably larger than the \( s_{1/2} \) state outside the bubble. Thus, we expect a blueshift of the \( D_1 \) transition, \( \Delta e^{(s_{1/2})} - \Delta e^{(p_{1/2})} > 0 \).

For \( p_{3/2} \) states, the situation is slightly more complicated because, in general, there are off-diagonal matrix elements among degenerate states with different \( m \). However, all the off-diagonal elements vanish if we assume that the helium atom lies on the \( Z \) axis, \( X = Y = 0 \), and \( Z = R \). We lose no generality in the case of a single helium atom. The helium atom at \( Z = R \) produces an energy shift \( \Delta e \) given by

\[
\Delta e^{(p_{3/2})} = \langle \psi^m(R) V_{e-He} \psi^m(R) \rangle = \begin{cases} 2 V_0 \rho_e^{(p_{3/2})} & \text{for } |m| = 1/2 \\ 0 & \text{for } |m| = 3/2, \end{cases}
\]

(2.20)

where \( \rho_e^{(k)} \) is the angle-averaged electron density. There is no shift for \( |m| = 3/2 \) states in the first-order perturbation by \( V_{e-He} \). As a result, the \( D_2 \) transition splits into two peaks: one has a blueshift, \( \Delta e^{(p_{3/2})} > 0 \), and the other has a small redshift, \( -\Delta e^{(p_{3/2})} < 0 \). In fact we can neglect \( -\Delta e^{(s_{1/2})} \) in comparison to the other shifts due to the large distance from the perturbing helium atom. Also one can neglect the small energy difference between the two spin-orbit partners. Then the energy shift of \( |m| = 1/2 \) is twice as large as that of \( p_{1/2} \) states. Note that the average shift of the \( D_2 \) components is the same as of the \( D_1 \) line. In summary, a helium atom at a distance \( R \) shifts the \( D_1 \) transition by \( \Delta = \rho_e^{(p_{3/2})}(R) \). The energy of the \( D_2 \) transition splits into two: one has no shift and the other is shifted by \( 2\Delta \). This explains qualitatively the overall blueshift of both lines and the skewed profile of the \( D_2 \) line.

However, while the observed \( D_2 \) line shape can be analyzed as a sum of two components, both components are blueshifted by roughly the same amount as the \( D_1 \) line. This shows that the shift is due to the simultaneous interaction with several helium atoms. For example, if two helium atoms are at \((R,0,0)\) and \((0,0,R)\), again a \( D_2 \) line splits into two. However, in this case, both have blueshifts \( \Delta \) and \( 3\Delta \). If three helium atoms are at \((R,0,0)\), \((0,R,0)\), and \((0,0,R)\), then the \( D_2 \) line shows a blueshift of \( 3\Delta \) but no splitting. Roughly speaking, the magnitude of the line shift is determined by the number of helium atoms contributing to the perturbation and the splitting is determined by anisotropy of the helium configuration, which increases as the square root of the number of atoms, assuming that there are no correlations between atoms. The average energy shift remains the same for the \( D_1 \) and \( D_2 \) lines, irrespective of the number of helium atoms causing the perturbation.

III. NUMERICAL RESULTS

To calculate the line shapes of the cesium \( D \) transitions in liquid helium, we evaluated Eqs. (2.17) and (2.18) by sampling 100 000 helium configurations, generated according to the density profiles in Fig. 1. The calculated energy shifts are added to the observed \( D \) lines of free Cs atom \((\lambda = 894.9 \text{ nm for } D_1 \text{ and } 852.7 \text{ nm for } D_2)\). Then, the intensity is estimated by counting the number of scatters in bins of wavelength \( \Delta \lambda = 0.1 \text{ nm} \). The obtained intensity spectra are shown in
Experimental observations have a double-peaked structure. This feature agrees with the broadening of the $D_0.3$ Å out of 6 Å would be sufficient to produce the measured wave function. About 10% error in the wave function would be required to reproduce the observed pressure dependence, but comes out about 20% lower than measured. The difference could be due to incorrect asymptotic wave function in the Cs atom; about 20% lower than measured. The difference could be due to incorrect asymptotic wave function in the Cs atom. The experimental data from Ref. [9] are plotted as filled squares.

Fig. 3. The $D_1$ line can be well approximated by a single Gaussian, although there is a slightly larger peak at the high-energy (low-wavelength) side. On the other hand, the $D_2$ line has a double-peaked structure. This feature agrees with experimental observations [9,10].

Figure 4 shows the pressure dependence of the peak shift and broadening of the $D_1$ excitation lines. The peak shift reproduces the observed pressure dependence, but comes out about 20% lower than measured. The difference could be due to an incorrect asymptotic wave function in the Cs atom; only a 10% error in the wave function would be required to explain the difference. Or the calculated helium bubble might be too large. Here, decreasing the size of the bubble by 0.3 Å out of 6 Å would be sufficient to produce the measured peak shift. We shall return to this later. The line broadening comes out better than would be expected, given the quality of agreement for the peak shift. The agreement here shows that the fluctuations of the helium distribution are well described by the model adopted.

A qualitative measure of the fluctuations can be constructed by defining an effective number of helium atoms that contribute to the perturbation. Calling the shift from an individual helium atom $\Delta(i)$, the total shift is

$$\Delta E = \sum_{i=1}^{N} \Delta(i).$$  (3.1)

The effective number of atoms $M_{eff}$ responsible for the shift may be defined as

$$M_{eff} = \left( \frac{\sum_{i} \Delta(i)}{\sum_{i} \Delta(i)^2} \right)^{1/2},$$  (3.2)

where $\langle \cdots \rangle$ indicates the ensemble average. The calculation leads to $M_{eff}\approx 8$ for the $s_{1/2}$ state at $P = 0$, increasing to 11–12 at $P = 25$ atm. The $M_{eff}$ can be compared with the number of helium atoms in the first shell of the density profile (Fig. 1). The average numbers of helium atoms in a region of $r < 8.5$ Å are 27 at $P = 0$ and 45 at $P = 25$ atm. $M_{eff}$ turns out to be much smaller than the number in the first shell. Therefore, we may say that the perturbation of the valence electron is dominated by a small number of helium atoms in the inner surface of a bubble. This fact indicates the importance of treating the perturbation from individual helium atoms in describing the fluctuation effect.

We can also understand the order of magnitude of the fluctuation effects using $M_{eff}$. Assuming independent helium atoms, the fluctuations are proportional to $1/\sqrt{M_{eff}}$. Thus we would expect that the widths of the lines and the splitting of the components of $D_2$ would be proportional to the average shift times that quantity. In fact, the $D_1$ width is about 1/2 its average shift in the zero-pressure data, to be compared with $1/\sqrt{M_{eff}}=1/3$. Reference [9] analyzes the $D_2$ line shape as a sum of two Gaussian peaks. For measurements at low pressure, the splitting of the components relative to the average shift is just 1/3, agreeing with our very crude argument.

In order to investigate effects of the polarization potential that we have so far neglected, we consider also a He-Cs interaction that includes the van der Waals terms [19]. Once the density profile $\rho(r)$ is determined, we use the interaction between a valence electron and helium, Eq. (2,6), to calculate the atomic spectrum. We find that the potential of Ref. [19] gives a reduced radius for the helium bubble at zero pressure, by about 0.3 Å. As a result, the blueshift increases by about 35 cm$^{-1}$ at $P = 0$, which fits the experimental data very well. The linewidth is also slightly increased. This enhancement of blueshifts diminishes as the pressure is increased. The calculation shows almost no additional shift at $P = 20$ atm.
Next, let us discuss effects of correlations among helium atoms. The He-He correlation should influence the linewidth because it removes some part of the fluctuations of the He configuration. Roughly speaking, the radial fluctuation controls the linewidth and the angle fluctuation determines the skewness of the $D_2$ line. To test this, we sample the helium configurations using the probability distribution of Eq. (2.14), taking $d = 2.377$ Å. We construct the distribution function $g(r)$ in Eq. (2.14), so as to reproduce the density profile $\rho(r)$ determined by the DFT, Eq. (2.9). The results are displayed in Fig. 5 and also in Fig. 4 with open squares. The correlation effect does not change the average peak positions at all. However, it reduces the linewidths, especially when the liquid helium is under high pressure. At $P = 20$ atm, the full width at half maximum of the $D_1$ line is calculated to be 150 cm$^{-1}$, which agrees well with the experiment (140 cm$^{-1}$). The skewness of the $D_2$ line is also decreased.

IV. SUMMARY

We have developed a simple model to describe the atomic spectra of impurities embedded in superfluid helium. Our description employs a density-functional theory for the helium distribution, and treats helium configurations statistically. The model is applied to the spectrum of cesium atoms embedded in superfluid helium. Various features in the spectrum, including line shifts, broadening, and skewness, are nicely reproduced in our calculation without any adjustable parameters. Thus, we are confident that our model includes the basic physical elements of the helium perturbation correctly. It will be interesting to see whether the model can also describe the emission spectra of atoms immersed in helium, and that will be a subject of future study. Since the model is simple enough to apply to more complex chromophores such as molecules and clusters, we also wish to analyze larger systems as well in the future.

ACKNOWLEDGMENTS

One of the authors (T.N.) thanks Y. Matsuo, Y. Fukuyama, and R. Sanetou for discussions. K.Y. acknowledges conversations with S. Ogata, and financial support by the Ministry of Education, Culture, Sports, Science and Technology of Japan, Contract No. 11640372. G.F.B. acknowledges conversations with P. G. Reinhard and J. Rehr, and support from the U.S. Department of Energy under Grant No. DE-FG06-90ER40561.