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A new fully quantum-mechanical method used to calculate the collisional broadening coefficients and shift coefficients of Rb D_1 lines perturbed by noble gases He and Ar*

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In this work, a new full quantum method is proposed to calculate the broadening and shift coefficients of the D_1 line in neutral collision. Based on the variable phase approach and Baranger theory, this method calculates the scattering phase shift instead of scattering matrix elements in order to simplify the calculation. As an illustration, this method is used to calculate the broadening and shift coefficients of the absorption lines of alkali metal atom Rb, as it collides with buffer gas He and Ar, in a temperature range from 150 K to 800 K. With a comparison with other calculations and experiment measurements, the reasonable agreements in all cases demonstrate the validity and simplicity of this method.

Keywords: collisional broadening and shift, variable phase method, phase shift

PACS: 32.70.Jz, 34.50.–s, 03.65.Nk **DOI:** 10.1088/1674-1056/27/1/013201

1. Introduction

More recent interest in the spectral broadening and shift of alkali metal atoms, as they collide with noble gases, has been inspired by applications in astrophysics,[1] the optically pumped alkali lasers (OPALs),[2] and the highly polarized neutron target.[3] For example, in astrophysics, the atmosphere of the brown dwarf stars consists of alkali metal and a lot of helium.[4] The collisional broadening of the alkali line can be used as a diagnostic tool for its environment, especially for understanding the particular compositions of observed stellar atmospheres.[4,5] For the OPAL, the alkali–buffer-gas mixture is used as a gain medium and the line broadening of the alkali enhances the absorption from the optical pump. A required optical pump source can be matched by controlling the pressure of buffer gas, making the OPAL achieve high power and high quality.[2,6] In highly polarized neutron target, the broadening is employed to calculate the number density of ^{3}He gas, which is necessary to determine the nuclear polarization.[3] The analysis and modeling of pressure broadening and shift of atomic spectral lines have been crucial for the spectroscopy.

At present, there are two primary physical models to deal with the broadening and shift of the collisional broadened spectral line shape, the semi-classical Anderson–Talman (AT) theory[7] and the quantum mechanical Baranger theory.[7–9] AT theory views atomic collision as a classical collision and utilizes a dipole autocorrelation formulation to describe the broadening and the shift. By this method, Blank L and Weeks D[10] calculated the broadening and shift coefficients of M = K, Rb, and Cs perturbed by N = He, Ne, and Ar over a temperatures range of 50–3000 K. As only the spectral line itself being treated quantum-mechanically, this approach is obviously incomplete.[7] The Baranger theory is a fully quantum-mechanical method. Baranger employed an impact approximation that pervaded his entire work, and expressed the broadening and shift of the spectral line in terms of quantum-mechanical scattering amplitudes.[8,9] Based on this model, Allard and Kielkopf developed a more general form from the scattering matrix elements.[7] Mullamphy *et al.*[4] calculated the scattering matrix elements from the asymptotic behavior of the radial wave functions to determine the broadening and shift coefficients for temperatures up to 3000 K for Li, Na, and K perturbed by He. Loper[11] also employed the method to calculate the broadening and shift coefficients of M = K, Rb, and Cs perturbed by N = He, Ne, and Ar for temperatures ranging from 100 K up to 800 K. In his work, the scattering matrix elements were computed by the channel packet method.[12] However, the calculations of the scattering matrix are complicated and time consuming, which motivate us to develop a new more intuitive and simpler method. Another theoretical motivation is to unfold the information of the potential energy surface, which governs collisions between alkali metal and noble gases.

For D_1 line of alkali atom perturbed by noble gas, only elastic scattering does exist. Thus, the scattering matrix elements can be replaced with the scattering phase shift, referring to a partial wave analysis of elastic scattering.[8] In this paper, we calculate the scattering phase shift by the variable phase method, to determine the broadening and shift coefficients. Due to its simplicity, the variable phase approach has been an attractive tool for understanding the scattering process,[13]

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and has been widely used such as calculations of the scattering lengths,[14] the detection of bound and meta-stable states,[15] and so on. In this work, we calculate the broadening and shift coefficients of Rb perturbed by He and Ar for temperatures from 150 K to 800 K. The details of our method are described in Section 2. Section 3 presents the potential energy curves we used. In Section 4, we summarize the calculated results, and compare the results with other calculations and experimental data. The discrepancy of our results and the efficiency of our calculation method are also discussed.

2. Computational method

2.1. Theory of spectral line broadening and shift

A general result of the half-width α and shift β at temperature T of the line core of the spectral Lorentzian profile has been deduced by Allard and Kielkopf as[7]

$$\alpha + \mathrm{i}\beta = n \int_0^\infty f(v)\, v \mathrm{d}v \int_0^\infty 2\pi b \mathrm{d}b \left(1 - S_{\mathrm{ff}}^{-1} S_{\mathrm{ii}}\right)_{\mathrm{Av}}, \tag{1}$$

where n is the perturber number density, $f(v)$ is the Maxwell velocity distribution of mutual perturber–radiator velocities, b is the impact parameter, $S_{\mathrm{ff}}^{-1}$and S_{ii} are the scattering matrix elements, the subscripts i and f denote the initial state and the final state of the radiator, respectively. The subscript Av is an average symbol over the ensemble of perturbers' states.

Refer to Baranger's approach,[8] the scattering matrix elements can be expressed in the form of scattering amplitude $S_{\mathrm{ii}} = f(\theta)$. By

$$b\mathrm{d}b = \frac{(2l+1)\,\mathrm{d}l}{2k^2} = \frac{(2l+1)}{2k^2}\,(\mathrm{d}l = 1),$$

the integration over the impact parameter b can be converted to a sum over the orbit angular momentum l. Thus, for a given angle θ, we can replace the integrations over impact parameter with the scattering amplitude as a sum over partial waves as

$$\int_0^\infty 2\pi b \mathrm{d}b f(\theta) = \sum_0^\infty 2\pi \frac{(2l+1)}{2k^2} f_l(\theta). \tag{2}$$

The scattering amplitude of each partial wave is described by

$$\begin{aligned} f_l(\theta) &= (\exp(2\mathrm{i}\delta_l(k)) - 1)\frac{(2l+1)}{2\mathrm{i}k}\mathrm{P}_l(\cos\theta) \\ &= (\exp(2\mathrm{i}\delta_l(k)) - 1)\frac{(2l+1)}{2\mathrm{i}k}, \end{aligned} \tag{3}$$

where $\mathrm{P}_l(\cos\theta) = 1$ because only the forward scattering is considered[8] and $\delta_l(k)$ is the scattering phase shift related to wave number k.

If we assume an ideal gas ($P = nk_{\mathrm{B}}T$, where k_{B} is the Boltzmann constant), and assume the velocity distribution to be a Maxwell average speed, then we can combine Eqs. (1)–(3) and use DeBroglie relation to find

$$\frac{\alpha}{P} = \frac{\pi\hbar}{\mu k k_{\mathrm{B}} T} \sum_{l=0}^{\infty} (2l+1)(1 - \cos 2\theta_l), \tag{4}$$

$$\frac{\beta}{P} = -\frac{\pi\hbar}{\mu k k_{\mathrm{B}} T} \sum_{l=0}^{\infty} (2l+1)\sin 2\theta_l, \tag{5}$$

where μ is the reduced mass of the radiator–perturber system, and the phase shift difference $\theta_l = \delta_l^{\mathrm{U}} - \delta_l^{\mathrm{L}}$, in which δ_l^{U} and δ_l^{L} represent the scattering phase shifts of upper and lower energy level of the emitter, respectively. In Eqs. (4) and (5), α and β are divided by the pressure P, respectively, so that we can calculate broadening and shift coefficients in the standard experimental units of MHz/torr.

Therefore, for atomic collisions between alkali atom and noble gas atom, the calculation on the scattering matrix elements can be translated into the calculation on the scattering phase shift to determine the width and shift of collisional spectral line.

2.2. Variable phase method

In a central force field collision process, we can deduce the radial Schrödinger equation as[13]

$$\frac{\mathrm{d}^2\chi_l(r)}{\mathrm{d}r^2} + \left[\frac{2\mu}{\hbar^2}(E - V(r)) - \frac{l(l+1)}{r^2}\right]\chi_l(r) = 0, \tag{6}$$

where $\chi_l(r)$ is the radial part of the wave function by expressing the total wave function as partial waves $\psi = \sum_{l=0}^{\infty} \chi_l(r)\mathrm{P}_l(\cos\theta)/r$, with $\hbar$ Planck constant, $V(r)$ the interaction potential, and E the system total kinetic energy.

When $r \to \infty$, the solution of Eq. (6) $\chi_l(r)$ approximately equals to

$$\chi_l(r) \propto \sin\left(kr + \delta_l - \frac{l\pi}{2}\right), \tag{7}$$

in which $k = \sqrt{2\mu E}/\hbar$ and δ_l is the scattering phase shift.[13]

Before and after a neutral collision, the radiator atom should be a free particle and the collision just changes the phase of wavefunction of the collisional partners. The difference of the phase is mainly resulted from the interaction potential. The potential can be divided into two sections as

$$U(r) = \begin{cases} U_\rho(r), & 0 \le r \le \rho, \\ 0, & r > \rho. \end{cases}$$

In the section $r > \rho$, equation (7) can be expressed as $\chi_{l_\rho}(r) \propto \sin(kr + \delta_l(\rho))$, because $\delta_l(\rho)$ is only related to the potential range ρ.

Let

$$X_\rho(r) = \frac{1}{\chi_{l_\rho}(r)} \frac{\mathrm{d}\chi_{l_\rho}(r)}{\mathrm{d}r},$$

then

$$X_\rho(r) = \frac{\cos(kr + \delta_l(\rho))}{\sin(kr + \delta_l(\rho))} k,$$

and

$$\frac{\mathrm{d}\delta_l(\rho)}{\mathrm{d}\rho}=\frac{\frac{\mathrm{d}X_\rho(r)}{\mathrm{d}\rho}\sin^2(kr+\delta_l(\rho))+k^2}{-k}.$$

In fact, the potential range ρ verges to infinity, namely, $V(r)$. Taking the boundary continuity of wavefunction into consideration, the relation of the scattering phase shift with atomic spacing r becomes

$$\frac{\mathrm{d}\delta_l(r)}{\mathrm{d}r}=\frac{\frac{\mathrm{d}X_\rho(r)}{\mathrm{d}r}\sin^2(kr+\delta_l(r))+k^2}{-k}. \tag{8}$$

Making use of

$$X_\rho(r)=\frac{1}{\chi_{l_\rho}(r)}\frac{\mathrm{d}\chi_{l_\rho}(r)}{\mathrm{d}r},$$

we can reduce the second-order differential equation (6) to a first-order differential equation as

$$\frac{\mathrm{d}X_\rho(r)}{\mathrm{d}r}+k^2-\frac{2\mu}{\hbar^2}V(r)-\frac{l(l+1)}{r^2}+X_\rho^2(r)=0. \tag{9}$$

Substituting Eq. (9) into Eq. (8), we derive the first-order variable phase differential equation of $\delta_l(r)$

$$\frac{\mathrm{d}\delta_l(r)}{\mathrm{d}r}+\frac{\frac{2\mu}{\hbar^2}V(r)+\frac{l(l+1)}{r^2}}{k}\sin^2(kr+\delta_l(r))=0. \tag{10}$$

Equation (10) requires an initial condition $\delta(r_0)$ to be propagated. To avoid the numerical instability, we set a starting point close to the origin as r_0, refer to Ref. [13]. When angular momentum is zero, there must be a point that satisfies $\chi_0(r_0)=0$. From Eq. (7), we can distinctly achieve the initial condition $\delta_0(r_0)=-kr_0$. Changing the angular momentum to larger values will shift the potential to the right, making this initial condition appropriate for any angular momentum. Then the initial condition is

$$\delta(r_0)=-kr_0. \tag{11}$$

The production of the phase shift entirely attributes to the system total potential including the interaction potential $V(r)$ and the centrifugal potential $l(l+1)/r^2$. In the case of interaction potential $V(r)=0$, the solution of Eq. (6) will expressed as a Riccati–Bessel function, in the form of $\sin(kr-(l\pi/2))$ and $\cos(kr-(l\pi/2))$. Consequently, the solution of Schrödinger equation itself for $V(r)=0$ will carry a phase shift $-l\pi/2$. Thus, the phase shift resulting from interaction potential should be achieved by subtracting $-l\pi/2$ from the solution of Eq. (10)

$$\delta_l=\lim_{r\to\infty}\delta_l(r)+\frac{l\pi}{2}. \tag{12}$$

Therefore, the calculation of the scattering phase shift could be summarized with the following:

$$\begin{aligned}&\frac{\mathrm{d}\delta_l(r)}{\mathrm{d}r}+\frac{\frac{2\mu}{\hbar^2}V(r)+\frac{l(l+1)}{r^2}}{k}\sin^2(kr+\delta_l(r))=0,\\&\delta(r_0)=-kr_0,\\&\delta_l=\lim_{r\to\infty}\delta_l(r)+\frac{l\pi}{2}.\end{aligned} \tag{13}$$

By solving Eq. (13), for every scattering channel l, the phase shift was computed. The phase shift difference of every channel was achieved by subtracting the phase shift of the ground state from the excited state. Then, we substituted the phase shift difference θ_l to Eqs. (4) and (5) to work out the broadening coefficients and shift coefficients, respectively.

Combining the Baranger theory with the variable phase method, we would achieve a new full quantum method to calculate the spectral width and shift. In the processing method, only the relative motion of alkali atom and noble gas atom changed, which corresponds to the quantum mechanics scattering physical process. An advantage of the method over the traditional method is that we only need to solve a first-order differential equation, which reduces the calculation steps and resources to a large extent. It shows the simplicity of this method.

3. Potential energy curves

From Eq. (10), the phase shift carries all information of the interaction potential that governs the collisions between alkali metal and noble gases, and it can be used to describe the collisional process completely. The main idea of the variable phase method is to define a potential energy analytical function $V(r)$. In this work, we utilized a more recent and general potential model to obtain the function $V(r)$, composed of the well-known long-range van der Waals terms and the short-range exponential repulsion, developed by Tang and Toennies.[16] For the D_1 lines of alkali perturbed by noble gas atom, $X^2\Sigma^+_{1/2}$ represents the system ground-state potential energy curves and $A^2\Pi_{1/2}$ represents the excited state.[17]

For the interaction potential between rubidium and helium, we made use of the latest calculation results by means of the one electron pseudo potentials method including spin–orbit interaction by Miller, who used the potential to make predictions and provided an excellent quantitative agreement with the experimental observations.[18] Through a least square fit, the parameters in the potential energy analytical function were extracted from Tang and Toennies model.[16] As shown in Fig. 1, for all inter nuclear distances, the discrepancy between the analytical function and the numerical potentials is $< 3\ \mathrm{cm}^{-1}$.

As the processing approach of rubidium and helium, we fitted out the analytical form of the potential energy function

for rubidium and argon, as shown in Fig. 2, and an excellent agreement can be observed. For all inter nuclear distances, the discrepancy between the analytical function and the numerical potentials is < 3 cm^{-1}. However, the numerical potentials that we employed were from the latest computation results of Blank,[17] who obtained them by using the *ab initio* method via a state-averaged multi-configurationally self-consistent field calculation followed by a spin–orbit multi-reference configuration interaction calculation.

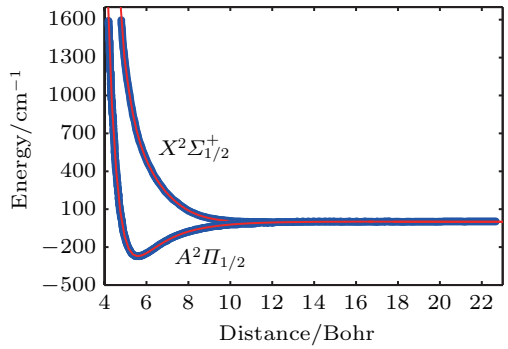


Fig. 1. (color online) The interaction potential energy curves of the ground state and the excited state of Rb and He, the blue spots denote the numerical potential from Ref. [18], while the red lines denote the fitted result.

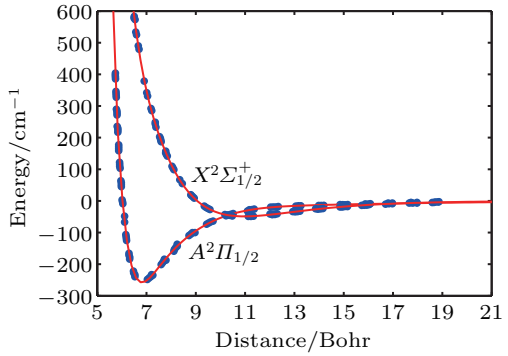


Fig. 2. (color online) The relationship between the interaction potential of the ground state and the excited state of Rb and Ar and their distance, the blue spots represent the numerical potential from Ref. [17], while the red lines represent the fitted result.

4. Results and discussion

4.1. Computation details

We use a Runge–Kutta sixth-order method to perform the numerical integration of Eq. (13) in atomic units. Propagation of variable phase equation for $k = 12$/Bohr will be displayed and discussed. The initial condition is 5.942 Bohr for excited state $A^2\Pi_{1/2}$ of Rb and Ar, but the convergence of the maximum integration coordinate should be tested.

For the minor angular momentum, the contribution of centrifugal potential will be ignored quickly as r increases. For example, in the case of $l = 0$, the phase shift will reach to a constant value as the potential energy converges to the maximum position which is nearly 25 Bohr, as shown in Fig. 3. However, for larger angular momentum values, the integration must be carried out in large scattering coordinates. To be more reasonable to cancel the centrifugal contribution, we imposed a condition as $l(l+1)/r^2 = 10^{-6}$, where the maximum integration coordinates can be estimated. For $l = 100$, we achieved the final integration position at $r = 10^5$ Bohr.

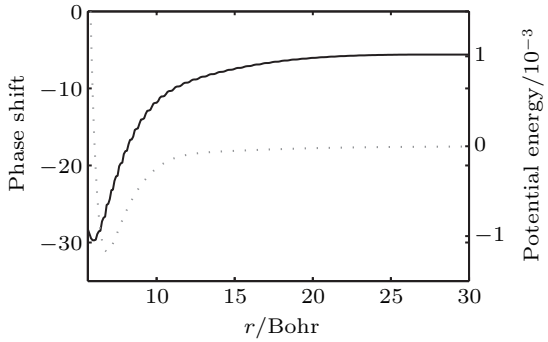


Fig. 3. For Rb and Ar, the phase shift (solid line) and the interaction potential in atomic units vary as scattering coordinate changes, the parameters used are $k = 12$/Bohr and $l = 0$.

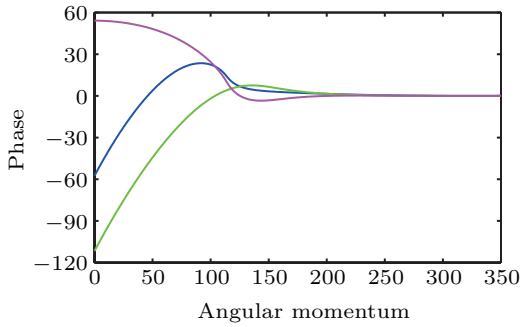


Fig. 4. (color online) The phase shift of the excited state $A^2\Pi_{1/2}$ (the blue line) and the ground state $X^2\Sigma^+_{1/2}$ (the green line) and the phase shift difference θ_l (the purple line) for every scattering channel of Rb and Ar, and the parameters used is $k = 12$/Bohr.

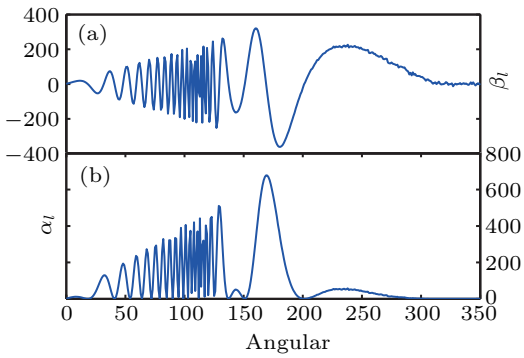


Fig. 5. (color online) The summation parts $\beta_l = (2l+1)\sin 2\theta_l$ of Eq. (4) for shift (a) and $\alpha_l = (2l+1)(1-\cos 2\theta_l)$ of Eq. (5) for width (b).

For every scattering channel l, we achieved the scattering phase shift of ground state $X^2\Sigma^+_{1/2}$ and excited state $A^2\Pi_{1/2}$ through the above method, respectively, as shown in Fig. 4. By subtracting the phase shift of the ground state from the excited state, the phase shift difference θ_l of every channel

was achieved and is shown in Fig. 4. The contributions of every channel of the summation parts of Eqs. (4) and (5) were obtained by substituting θ_l into them, as shown in Fig. 5. Then the broadening and shift coefficients were calculated by the summation parts multiplying the coefficients of Eqs. (4) and (5), respectively.

4.2. Feasibility of the variable phase method

The production of the phase shift entirely attributes to the system total potential including the interaction potential $V(r)$ and the centrifugal potential $l(l+1)/r^2$. As the angular momentum increases, the centrifugal potential will exert an increasingly important effect and the phase shift produced by the centrifugal potential will become more important than the interaction potential. When the angular momentum increases to a certain value, the interaction potential will be negligible and the total potential will almost entirely come from the centrifugal potential. As a consequence, the phase shift $\lim_{r\to\infty}\delta_l(r)$ approximately equals to $-l\pi/2$ and the contribution from interaction potential will close to zero. In Figs. 4 and 5, we can clearly observe when the quantum number of orbit–angular momentum l exceeds 300, the phase shifts of the ground state and the excited state are both close to zero.

The reliability of the present calculation method can be inferred by comparing the maximum value of angular momentum with semi-classical output. We can estimate the maximum angular momentum from the relationship between impact parameter b and angular momentum l, namely $\sqrt{l(l+1)} = kb$ where $k = 12$/Bohr. From Fig. 3 about the interaction potential of Rb and Ar, the maximum impact parameter b can be estimated to be equal to the interaction potential range at a rough value 25 Bohr, so we approximately estimated the maximum of angular momentum to 300, above which there would be no scattering taking place. It is accorded with our numerical calculation output as shown in Figs. 4 and 5, which confirms the feasibility of our calculation method.

4.3. The computation results

Our calculation method is based on the Baranger theory, which begins with an impact approximation, the limit of low density of buffer gas or the limit in which the collisional duration time is far smaller than the time of collisions.[7–9] The approximation means that the transition between the excited state and the ground state is not affected by the perturbations at all. For D_1 line of alkali perturbed by noble gas, the radiator–perturber diatomic system possesses only one excited potential energy curve. Refer to Lewis,[19] the fine-structure transitions between excited states during the collision do not exist, which implies that both the Coriolis coupling effect and the non-adiabatic effect are unnecessary to be considered. Our calculations were made with no approximations beyond those of the impact limit in accordance with Baranger theory aside from the limits imposed by the Maxwell average speed we used.

By the new method, we calculated the broadening and shift coefficients for Rb D_1 line perturbed by He in a temperature range from 100 K to 800 K, using the thermal average energy. The precision of the present calculations is checked by comparing with available experimental values and theoretical outputs of Loper and Blank. Loper used the fully quantum-mechanical Baranger theory together with channel packet method[11] and Blank used the semi-classical AT theory.[10] Both of them also used the thermal average energy. In the current experimental values, only under several temperatures measurements were done.[20–23] The results and the comparisons of broadening and shift coefficients are showed in Figs. 6 and 7, respectively. Referring to Blank and Loper, we fit the results by a power law given by cT^d with fitting parameters c, d and the coefficients of determination (DC) characterizing the accuracy of the fitting model list in Table 1. We can find that the broadening coefficients we calculated are closer to experimental results and the shift coefficients provide a fair description of experimental measurements.

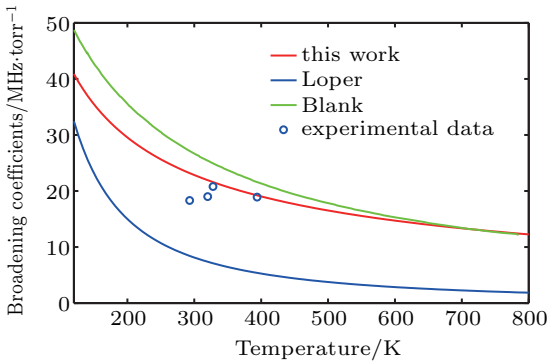


Fig. 6. (color online) A comparison of broadening coefficients computed using the new method for Rb +He in a series of temperatures with other theoretical calculations of Blank[10] and Loper.[11] A comparison with measurements in temperatures of 293 K,[20] 320 K,[21] 328 K,[22] and 394 K.[23]

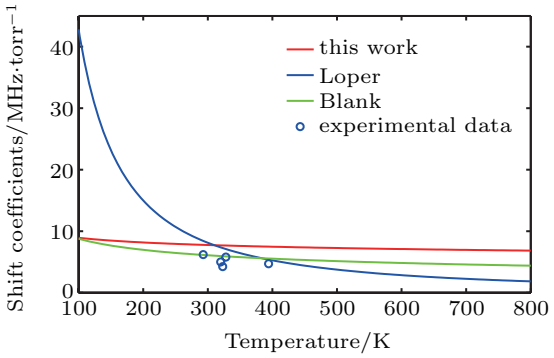


Fig. 7. (color online) A comparison of shift coefficients as described in Fig. 6.

In the same way, we also calculated the broadening coefficients and the shift coefficients, for Rb D_1 line per-

turbed by Ar in a series of temperatures, and compared with other theoretical calculations[10,11] and experimental measurements,[20,21,23] as shown in Figs. 8 and 9, respectively. The parameters and the determination coefficients (DC) of the fitting function cT^d are listed in Table 2. It is found that the broadening coefficients we calculated show good predictions of experimental values and our calculated shift coefficients show a particularly excellent connection with experimental results.

Table 1. Results of fitting broadening and shift coefficients of Rb and He to a cT^d function and the coefficients of determination (DC), and the comparison with Loper and Blank. The parameter c is in the unit of 10^4 MHz/torr and T is in Kelvin ranging from 100 K to 800 K.

	Broadening			Shift		
	c	d	DC	c	d	DC
This work	0.0834	−0.642	0.9783	0.0016	−0.1277	0.9735
Loper[11]	4.5109	−1.511		3.5289	−1.5178	
Blank[10]	0.1553	−0.716		0.004	−0.3328	

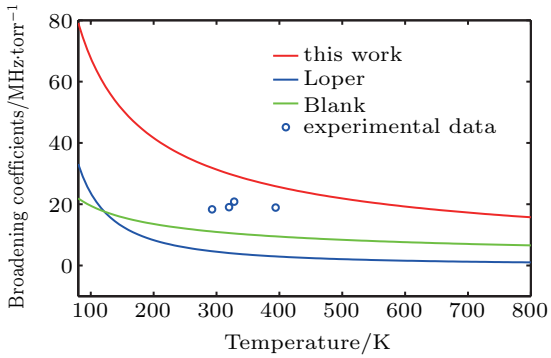


Fig. 8. (color online) A comparison of broadening coefficients we computed for Rb+Ar in a series of temperatures with other theoretical calculations of Blank[10] and Loper,[11] and a comparison with measurements at temperatures of 293 K,[20] 320 K,[21] and 394 K.[23]

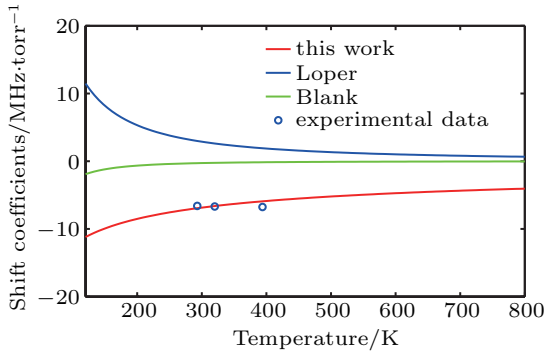


Fig. 9. (color online) A comparison of shift coefficients for Rb+Ar as described in Fig. 8.

Table 2. Results of fitting broadening and shift coefficients of Rb and Ar to a cT^d function and the coefficients of determination (DC), and the comparison with Loper and Blank. The parameter c is in the unit of 10^4 MHz/torr and T is in Kelvin ranging from 100 K to 800 K.

	Broadening			Shift		
	c	d	DC	c	d	DC
This work	0.1713	−0.7017	0.9878	−0.0146	−0.5356	0.9846
Loper[11]	2.4984	−1.5122		1.5597	−1.5071	
Blank[10]	0.0218	−0.5242		−4.6248	−2.1075	

From the trend in Figs. 6 and 7 and the parameters d in Table 1 of Rb and He, our results have a similar tendency as those of Blank especially for larger temperatures. Owing to the relatively large mass of an atom the relative motion of the heavy particle in a collision is nearly classical and the orbit is nearly a straight line.[24,25] Using the classical path approximation, the phase shift difference θ can be expressed by[26]

$$\theta = 2\pi \frac{c}{v} \int_{-\infty}^{\infty} \Delta V \left(y^2 + b^2\right)^{1/2} \mathrm{d}y,$$

as in the Anderson–Talman model used in Blank. It is the reason why our results of Rb and He are similar to Blank's. However, for Rb and Ar, the classical path approximation has been failed because of the relatively smaller mass difference between them.

Compared with the results of Loper, who used the fully quantum-mechanical method by solving the scattering matrix elements, our results have a significant difference, especially for Rb and Ar. The main source is because of the differences between different methods. Different processing method or approximation will bring evident differences in the final results, as introduced by Peach.[27] Moreover, as described in Loper's work, a system with the heavier reduced mass requires a larger momentum space, which lead to a limitation in computation resource and a significant error,[11] However, this situation does not exist in our method.

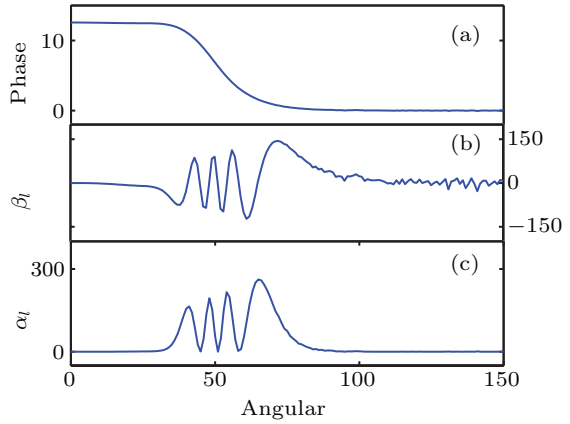


Fig. 10. (color online) The phase shift difference θ_l (a) for every scattering channel, β_l for shift (b) and α_l for width (c) (as described in Fig. 5), of Rb and He, and the parameters used is $k = 7.5$/Bohr.

In this work, there are several potential sources of error. In Section 3, the discrepancy of the analytical function and the numerical results of the interaction potential is < 3 cm^{-1}. Any error in the interaction potential will be reflected in the final results. Meanwhile, the slight difference of potential will also lead to an obvious difference in the results, as depicted by Allard.[28] In some way, the implementation of the analytical function may be flawed because of the fitting error, which suggests us to use a better fitting model. Another error is the

inevitable numerical noise in the phase propagation process of Eq. (13). In particular, when the phase shift is near zero, that is in the case of large angular momentum, the effect of the noise will become more obvious, see the trailing parts of β_l curves in Figs. 5(a) and 10(b) for He and Ar, respectively. Comparing Fig. 5 with Fig. 10, on the premise of the same calculation accuracy, for Rb and He, the relatively smaller reduced mass will have a greater impact of the noise. Moreover, for large angular momentum, the difference of the phase shift θ_l is so small that $\sin(\theta_l) \approx \theta_l$ and $\cos(\theta_l) \approx 0$. The small but nonzero difference will result in the integrand (5) to remain nonzero but the integrand in Eq. (4) to vanish. Thus, we can observe the numerical noise affects the shift β_l more than the broadening α_l, as shown in the trailing parts of β_l and α_l curves of Figs. 5 and 10.

This core of this new method is to calculate the scattering phase shift which is mainly related with the interaction potential. The interaction potential we used includes the long-range van der Waals terms and an exponential short-range repulsion. The broadening coefficients mostly depend on the short-range repulsion potential, while the shifting coefficients are primarily sensitive to the long-range potential, which have been confirmed in other work.[4,10] According to our result, the interaction potential of Rb and He may need further improvement. However, in view of the good agreement of the shift coefficients and the poor agreement of the broadening coefficients of Rb and Ar with the experimental results, we suggest that the repulsive region of the interaction potential of Rb and Ar may need to be slightly suppressed.

In general, there is a reasonable agreement on both the broadening and the shift coefficients of our calculations with other theoretical calculations and experiments, no matter for D_1 line of Rb perturbed by He or by Ar. For the simple system, the validity and reliability of this new method are further validated. In addition, an advantage of this full quantum method over the traditional method is embodied in that we only need to solve a first-order differential equation. However, for more complex system, the feasibility of this method has yet to be tested.

5. Conclusion and perspectives

We proposed a new fully quantum-mechanical calculation method for the broadening and shift of alkali metal spectral line, based on the variable phase approach and the Baranger theory. The method exhibits reliable and simpler characteristics. Using this method, we calculated the broadening and the shift coefficients of Rb D_1 lines perturbed by He and Ar in a series of temperatures. The results are compared with experimental measurements and other theoretical calculations. In general, our results provide a better prediction of the broadening coefficients of Rb perturbed by He and Ar, and provide a fair prediction of the shift coefficients of Rb perturbed by He, and provide an excellent prediction of the shift coefficients of Rb perturbed by Ar. The general agreement in all cases demonstrates the validity and simplicity of this method. As a consequence, comparisons between various theories and experiment measurements should be made over a wider range of temperatures as much as possible, and our calculation method needs to be further confirmed in more complex situations.

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