Contrib. Astron. Obs. Skalnaté Pleso **50**, 193 – 202, (2020)
https://doi.org/10.31577/caosp.2020.50.1.193

The resonance lines of sodium and potassium in brown dwarf spectra

G. Peach[1], S. Yurchenko[1], K. Chubb[2], I. Baraffe[3], M. Phillips[3] and P. Tremblin[4]

[1] *Department of Physics and Astronomy, University College London WC1E 6BT, UK*
(E-mail: g.peach@ucl.ac.uk)
[2] *SRON, Netherlands Institute for Space Research*
[3] *Department of Physics and Astronomy, University of Exeter, UK*
[4] *Maison de la Simulation CEA Saclay, Paris*

Received: August 14, 2019; Accepted: September 12, 2019

Abstract. Accurate pressure broadened line profiles of alkali resonance doublets are needed for the modelling of atmospheres of cool stars and for generating their synthetic spectra in the region 400 - 900 nm. When the lines utterly dominate their region of the spectrum, it becomes important to represent the profiles accurately over the whole range from the line centre to the far line wings. In this paper we examine the theories of spectral line shapes that have been used and carry out new calculations of the line shapes for the resonance lines of sodium and potassium broadened by helium.

Key words: spectral line broadening calculations – alkali resonance doublets – cool stars: synthetic spectra

1. Introduction

The cool atmospheres of brown dwarfs are characterised by the formation of molecules and condensates. The highly wavelength dependent opacity of abundant molecules such as water, methane and ammonia dominate the infrared spectra of these substellar objects, while at shorter wavelengths the spectrum is shaped by the neutral alkali metals as more refractory elements are sequestered in condensate species. In particular the sodium and potassium resonance doublets, centered at 0.59 and 0.77 microns respectively, play a unique role in shaping the spectrum between 0.4-1.0 microns. H_2 and He are present at high atmospheric densities in the range ($\sim 10^{19}$ - 10^{21} cm^{-3}) and they collisionally broaden the resonance lines at wavenumbers up to $\pm 3000\,\mathrm{cm}^{-1}$ from the line centre.

Using our state-of-the-art 1D radiative-convective equilibrium model ATMO, we are developing a grid of model substellar atmospheres and investigating the impact of Na and K line shapes on predicted brown dwarf spectra. We find that there are large differences between the various published line shape calculations

and this can affect the predicted spectra. Most notably these uncertainties occur in the near-infrared due to the extent of the red wing of the K resonance lines.

Previous calculations have used various theories to obtain line shapes for alkali resonance lines broadened by helium. In the centre of the line the profile is Lorentzian, and half-half widths have been obtained for lithium, sodium and potassium broadened by helium, see Mullamphy et al. (2007), Peach and Whittingham (2009) and Kielkopf et al. (2012). Quasistatic theory has been used by Burrows and Volobuyev (2003) and Beuc et al. (2018) to describe the behaviour in the far line wings. A unified theory developed by Allard et al. (1999) is used by Allard et al. (2003) to obtain line profiles for a wide range of frequencies.

In this paper, an alternative method for obtaining complete line profiles is described and is applied to the resonance lines of sodium and potassium broadened by helium.

2. The Hamiltonian for the atom-perturber system

Large quantum chemistry calculations provide very accurate potentials for the electronic states of atom-atom systems at short and intermediate separations. This approach is limited to low excited electronic states. The present problems involve low-energy atom-atom scattering processes for excited electronic states. Our requirement is for the accurate representation of potentials at medium and large interatomic separations.

In this work a three-body model is adopted; two atomic cores a and b and one active electron, i.e. Na^+ + He + e^- and K^+ + He + e^-. Atomic units are used, with lengths in Bohr radii, $a_0 = 0.0529177209$ nm and energies in Hartrees, $E_h = \alpha^2 m_e c^2 = 27.211384$ eV.

The electron-core interaction is specified by

$$V_{a,b}(r) = -\frac{Z}{r}(1 + \delta + \delta' r)\exp(-\gamma r) - \frac{z}{r} - \frac{\alpha_d^{a,b}}{2r^4}\, F_1(r)\,, \tag{1}$$

where r is the electron-core separation, $Z + z$ is the nuclear charge, α_d^a and α_d^b are the dipole polarisabilities of the cores a and b and $F_1(r)$ is a cutoff factor. Parameters γ, δ and δ' are varied to reproduce the positions of known energy levels for $z \neq 0$, and phase shifts for scattering for $z = 0$. The fits also predict the correct number of nodes in the wave functions, see Peach (1982).

The core-core interaction is given by

$$V_c(R) \simeq -z_a^2\,\frac{\alpha_d^b}{2R^4} - z_b^2\,\frac{\alpha_d^a}{2R^4} + \text{short-range terms}\,, \tag{2}$$

where R is the separation between the two cores a and b with charges z_a and z_b respectively. Options considered for the short-range term are:

(a) Use the three-body model itself to generate the potential.

(b) Use a simple analytic form based on perturbation theory.

Choices (a) and (b) differ only for $R \leq R_A + R_B$ where R_A and R_B are the mean radii of Na^+ and K^+.

The three-body interaction is given by

$$V_3(\mathbf{r_a}, \mathbf{r_b}, \mathbf{R}) \simeq z_b \frac{\alpha_d^a}{r_a^2 R^2} P_1(\hat{r_a} \cdot \hat{R}) + z_a \frac{\alpha_d^b}{r_b^2 R^2} P_1(-\hat{r_b} \cdot \hat{R}) \tag{3}$$

for R large, where $\mathbf{r_a}$ and $\mathbf{r_b}$ are the position vectors of the electron relative to the atomic cores a and b. $\mathbf{R} = (\mathbf{r_a} - \mathbf{r_b})$ and $P_1(\hat{r} \cdot \hat{R})$ is a Legendre polynomial.

On using (1), (2) and (3), the Hamiltonian for the system then becomes

$$H = -\frac{1}{2}\nabla^2 + V_a(r_a) + V_b(r_b) + V_c(R) + V_3(\mathbf{r_a}, \mathbf{r_b}, \mathbf{R})\,. \tag{4}$$

A set of atomic basis states on one or both centres is used and the Hamiltonian matrix diagonalized to obtain the electronic energies.

The principles and problems involved in the construction of the potentials are:
(a) The long-range interactions are based on well-known perturbation theory.
(b) No existing data for the molecules NaHe and KHe are used to fix any variable parameters.
(c) Positions of virtual states in the electron-core model potentials are sensitive to the precise fit.
(d) Model potentials can be l-dependent or l-independent.
(e) A different potential may have to be used for ground states, e.g. He($1s^2$).

3. Theory of spectral line broadening

3.1. Baranger theory

The main references for the discussion that follows are Baranger (1958) and Peach and Whittingham (2009). The impact theory has been widely used, but is actually only an approximation to the general theory developed by Baranger in this his first important paper.

The line profile $I(\omega)$ is defined in terms of a correlation function $C(s)$ by

$$I(\omega) = \mathcal{R}\,\frac{1}{\pi}\int_0^\infty C(s)\exp(\mathrm{i}\Delta\omega s)\,\mathrm{d}s\,, \tag{5}$$

where ω is the angular frequency, $\Delta\omega$ is the angular frequency separation from the line centre and s is a time variable. $\mathcal{R}$ denotes 'real part of'. Baranger showed that $C(s)$ can be written as

$$C(s) = \exp[-N\,g(s)]\,, \tag{6}$$

where N is the perturber density and $g(s)$ is split into two parts, i.e.

$$g(s) = g_1(s) + g_2(s). \tag{7}$$

Only the first term $g_1(s)$ is used here as in many circumstances the second term, $g_2(s)$, can be neglected.

We consider the transition $n_i L_i \to n_f L_f$ between states $n_i L_i M_i$ and $n_f L_f M_f$ of the alkali atom. The wave function describing the scattering by a potential $V_\Lambda(r)$ is given by

$$\psi_\Lambda(\mathbf{r}) = \sum_{l=0}^{\infty} (2l+1)\, \mathrm{i}^l \exp(\mathrm{i}\eta_{\Lambda l}) \frac{1}{k^{\frac{1}{2}} r} F_{\Lambda l}(k,r)\, P_l(\hat{k}\cdot\hat{r})\,, \tag{8}$$

where $P_l(\hat{k}\cdot\hat{r})$ is a Legendre polynomial and the radial functions $F_{\Lambda l}(k,r)$ are solutions of the equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} - 2MV_\Lambda(r) + k^2\right] F_{\Lambda l}(k,r) = 0\,. \tag{9}$$

The potential $V_\Lambda(r)$ and the atom-atom separation r are in atomic units and M is the reduced mass of the emitter-perturber pair in units of the electron mass m. The momentum k in atomic units is given by

$$k = \frac{Mmva_0}{\hbar}\,, \tag{10}$$

where v is the relative velocity of the emitter and perturber and a_0 is the Bohr radius. The asymptotic form of $F_{\Lambda l}(k,r)$ is specified by

$$F_{\Lambda l}(k,r) \simeq k^{-\frac{1}{2}} \sin(kr - \frac{1}{2}l\pi + \eta_{\Lambda l})\,, \tag{11}$$

where $\eta_{\Lambda l} \equiv \eta_{\Lambda l}(k)$ is the elastic scattering phase shift, and as $r \to 0$

$$F_{\Lambda l}(k,r) \propto r^{l+1}\,. \tag{12}$$

For the cases considered here, the scattering matrix elements S_i and S_f are given by

$$S_i \equiv \langle l\Lambda_i|S|l\Lambda_i\rangle = \exp(2\mathrm{i}\eta_{\Lambda_i l})\,; \quad \Lambda_i = |M_i| \tag{13}$$

and

$$S_f \equiv \langle l\Lambda_f|S|l\Lambda_f\rangle = \exp(2\mathrm{i}\eta_{\Lambda_f l})\,; \quad \Lambda_f = |M_f|\,. \tag{14}$$

Then we obtain

$$N\, g_1(s) = (w + \mathrm{i}d)\, s\,, \tag{15}$$

where

$$w + \mathrm{i}d = \mathcal{C}\,\frac{\lambda^{1/2}}{M^{3/2}}\sum_{M_i M_f \mu}\begin{pmatrix} L_i & 1 & L_f \\ M_i & \mu & M_f \end{pmatrix}^2 \int_0^\infty \exp(-u)\,\mathrm{d}u \times \sum_{l=0}^{\infty}(2l+1)\,\{\mathrm{i}\,\exp[\mathrm{i}(\eta_{\Lambda i} - \eta_{\Lambda f})]\} \times [\,2M\int_0^\infty F_{\Lambda_i l}(k,r)\,\Delta V\,F_{\Lambda_f l}(k,r)\,\mathrm{d}r] \tag{16}$$

and $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ is a 3-j coefficient.

The quantities introduced here are defined by

$$\Delta V = V_{\Lambda_i} - V_{\Lambda_f} \tag{17}$$

and

$$\mathcal{C} = N\,4\sqrt{\pi}\,\frac{\hbar a_0}{m}\,; \quad u = \frac{E}{\kappa T} = \frac{\lambda k^2}{M}\,; \quad \lambda = \frac{\hbar^2}{2ma_0^2\kappa T}\,, \tag{18}$$

where κ is the Boltzmann constant, T is the temperature and E refers to the energy of the relative motion. All the dimensional information is contained in the factor $\mathcal{C}$. It then follows from (5), (6), (15) and (16) that w and d are the half-half width and shift of the Lorentz profile given by

$$I(\omega) = \frac{1}{\pi}\,\frac{w}{(\Delta\omega - d)^2 + w^2}\,. \tag{19}$$

3.2. The impact approximation

The well-known impact theory is obtained directly from (16) by replacing the wave functions $F_{\Lambda_i l}(k,r)$ and $F_{\Lambda_f l}(k,r)$ by their asymptotic forms (11), so that

$$w + \mathrm{i}d = \mathcal{C}\,\frac{\lambda^{1/2}}{M^{3/2}}\sum_{M_i M_f \mu}\begin{pmatrix} L_i & 1 & L_f \\ M_i & \mu & M_f \end{pmatrix}^2 \int_0^\infty \exp(-u)\,\mathrm{d}u \times \sum_{l=0}^{\infty}(2l+1)\,\frac{1}{2}[1 - S_i S_f^*]\,. \tag{20}$$

In addition, if the Born approximation is made, the phase shifts in (11) are calculated from the expression

$$\tan(\eta_{\Lambda l}) = -2Mk\int_0^\infty r^2 V_\Lambda(r)\,[j_l(kr)]^2\,\mathrm{d}r \tag{21}$$

for all values of l. In (21), $j_l(kr)$ is a spherical Bessel function of the first kind where

$$kr\,j_l(kr) \simeq \sin(kr - \frac{1}{2}l\pi) \tag{22}$$

as $r \to \infty$, c.f. (11). The Born impact theory is then obtained directly from equations (13), (14) and (20).

3.3. The one-perturber approximation

Finally we consider the one-perturber approximation. We define the quantity

$$P(\omega) = \int_0^\infty F_{\Lambda_i l}(k_i, r)\mathcal{D}(r)F_{\Lambda_f l}(k_f, r)\,\mathrm{d}r\,; \qquad \mathcal{D}(r) \equiv \frac{D(r)}{D(\infty)}\,, \tag{23}$$

where in general, $k_i \neq k_f$. The dipole moment for the transition $\Lambda_i \rightarrow \Lambda_f$ is $D(r)$, which tends to a constant, $D(\infty)$, as $r \rightarrow \infty$. Then $P(\omega)$ is given by

$$\begin{aligned}(k_i^2 - k_f^2)\,P(\omega) &= 2M \int_0^\infty F_{\Lambda_i l}\,\Delta V\,\mathcal{D}\,F_{\Lambda_f l}\,\mathrm{d}r \\ &- \int_0^\infty \frac{\mathrm{d}\mathcal{D}}{\mathrm{d}r}\left(F_{\Lambda_i l}\frac{\mathrm{d}F_{\Lambda_f l}}{\mathrm{d}r} - F_{\Lambda_f l}\frac{\mathrm{d}F_{\Lambda_i l}}{\mathrm{d}r}\right)\mathrm{d}r\,,\end{aligned} \tag{24}$$

where

$$(k_i^2 - k_f^2) = \frac{2mMa_0^2}{\hbar}\,\Delta\omega\,. \tag{25}$$

We now neglect the second term on the right-hand side of (24), as experience shows that it is negligible compared with the first term. The profile in the line wings is then given by

$$L(\omega) = [P(\omega)]^2 \tag{26}$$

and we obtain

$$I(\omega) \simeq \frac{1}{\pi}\,\frac{w}{\Delta\omega^2}\,; \qquad |\Delta\omega| \gg w\,, \quad |\Delta\omega| \gg |d|\,. \tag{27}$$

If the ranges of validity of the Baranger theory and the one-perturber approximations overlap, then the correlation function $C(s)$ can be replaced by

$$C(s) = 1 - N\,g_1(s) \tag{28}$$

and we can use these equations to obtain a unification of the two profiles $L(\omega)$ and $I(\omega)$.

Then the Lorentz profile in (19) is replaced by

$$I(\omega) = \frac{1}{\pi}\,\frac{w(0)}{(\Delta\omega - d)^2 + w(0)^2}\,\frac{w(\Delta\omega)}{w(0)}, \tag{29}$$

where

$$\begin{aligned}w(\Delta\omega) = \mathcal{C}\,\frac{\lambda^{1/2}}{M^{3/2}} \sum_{M_i M_f \mu} \begin{pmatrix} L_i & 1 & L_f \\ M_i & \mu & M_f \end{pmatrix}^2 \int_0^\infty \exp(-u)\,\mathrm{d}u \\ \times \sum_{l=0}^{\infty}(2l+1)\,[\,2M \int_0^\infty F_{\Lambda_i l}(k_i, r)\,\Delta V\,F_{\Lambda_f l}(k_f, r)\,\mathrm{d}r]^2\,,\end{aligned} \tag{30}$$

and

$$u = \frac{\lambda k_i^2}{M}\,. \tag{31}$$

If the wave functions in (30) are replaced by their asymptotic forms and we set $k_i = k_f$, $\Delta\omega = 0$. Then in (30) $w \equiv w(0)$ and $w(0)$ is identical with the expression for w given by (20).

This procedure will be valid for lower perturber densities, but will break down at high densities when the correlation function $C(s)$ in (6) must be evaluated directly and the Fourier transform in (5) performed.

4. Results and discussion

Calculations have been completed for the widths of the sodium and potassium resonance lines broadened by helium using the interaction potentials described in earlier work, see Mullamphy et al. (2007) and Peach (2011). The extensive temperature range chosen, 100 K $\leq T \leq$ 10000 K, serves two purposes. It provides the data required for the analysis of the spectra of cool stars, but also tests the range of validity of the various theoretical approximations discussed in this paper.

The main computational issues arise from the slow convergence of the sum over angular momenta l for the higher temperatures and the associated requirement for a greater number of points to be chosen for the integration over energy.

The radia1 equation describing the scattering wave function is integrated directly to determine the exact wave functions and their phase shifts for smaller values of l, $l \leq l_0$ say, and the Born approximation is then used to evaluate phase shifts for $l_0 < l \leq l_{max}$. The Born approximation for the scattering amplitude in its closed form is used to complete the summation up to $l = \infty$. Careful checks are made to determine the optimum values of l_0 and l_{max} at each energy.

Our results are shown in Tab. 1-Tab. 4. In Tab. 1 and Tab. 2 the half-half widths, $w(0)$, and shifts d are shown for the resonance lines of sodium and potassium. The results for $w(0)$ using the one-perturber and Baranger theories are compared and there is close agreement over the whole temperature range. In Tab. 3, the present results for $w(0)$ for sodium and potassium are compared with the earlier close-coupling calculations of Mullamphy et al. (2007) who use the impact approximation. There is very close agreement for the sodium lines; the agreement for the potassium lines is slightly less good, but this can be attributed to the fact that a small modification to the K-He potential was introduced in the present work.

Finally in Tab. 4, $w(\Delta\omega)/N$ is listed for sodium as a function of wavenumber $wnu = \Delta\omega/(2\pi c)$ to demonstrate the asymmetry in the line when the profile is extended out to the far wings.

5. Conclusions

In the present calculations we have demonstrated that the formalism and the computational techniques that have been developed can be successfully applied to obtain complete line profiles from the line centre to the line wings for all temperatures and for the lower perturber densities for which the one-perturber approximation is valid. The one-perturber term, $w(\Delta\omega)/N$, is generated for a wide range of values of temperature T(K) and $\Delta\omega$ which can then be interpolated to provide input into the atmospheric models.

Table 1. $w(0)/N$ and d/N (in units of 10^{-21}MHz m^3/atom) for the transition Na $3p^2P$–$3s^2S$ at 589.36 nm

T(K)	One-perturber $w(0)/N$	Baranger $w(0)/N$	Theory d/N
100.0	0.1741	0.1733	-0.0303
200.0	0.2310	0.2306	-0.0343
300.0	0.2713	0.2711	-0.0368
500.0	0.3319	0.3318	-0.0407
700.0	0.3792	0.3791	-0.0433
1000.0	0.4373	0.4372	-0.0457
1500.0	0.5146	0.5146	-0.0483
2000.0	0.5775	0.5775	-0.0502
2500.0	0.6314	0.6314	-0.0517
3000.0	0.6789	0.6789	-0.0529
5000.0	0.8307	0.8307	-0.0570
10000.0	1.0855	1.0855	-0.0622

A grid of model substellar atmospheres is being developed and these new profiles for the Na and K resonance lines will be incorporated into the models. We also intend to include the contribution from transitions where the emitter-perturber system occupies a bound state supported by the initial or final potentials for the molecular states Λ_i and Λ_f. These are known to contribute in the far red wings of the lines considered in this paper.

Table 2. $w(0)/N$ and d/N (in units of 10^{-21}MHz m^3/atom) for the transition K $4p^2P$–$4s^2S$ at 767.83 nm

T(K)	One-perturber $w(0)/N$)	Baranger $w(0)/N$	Theory d/N
100.0	0.1979	0.1979	-0.0325
200.0	0.2713	0.2713	-0.0378
300.0	0.3233	0.3233	-0.0380
500.0	0.3986	0.3986	-0.0359
700.0	0.4551	0.4551	-0.0341
1000.0	0.5222	0.5222	-0.0329
1500.0	0.6101	0.6100	-0.0334
2000.0	0.6819	0.6813	-0.0353
2500.0	0.7446	0.7427	-0.0377
3000.0	0.8012	0.7971	-0.0402
5000.0	0.9861	0.9702	-0.0490
10000.0	1.2808	1.2504	-0.0620

Table 3. $w(0)/N$ (in units of 10^{-21}MHz m^3/atom) [a]Mullamphy et al. (2007), [b]present work

atom	T(K)	$w(0)/N^a$	$w(0)/N^b$
Sodium			
	450.0	0.3167	0.3166
	480.0	0.3252	0.3257
	1000.0	0.4367	0.4372
	2000.0	0.5781	0.5775
	3000.0	0.6813	0.6789
Potassium			
	410.0	0.3463	0.3647
	1000.0	0.5032	0.5222
	2000.0	0.6799	0.6813
	3000.0	0.8109	0.7971

Table 4. $w(\Delta\omega)/N$ (in units of 10^{-21}MHz m^3/atom) for the transition Na $3p^2P$–$3s^2S$ at 589.36 nm at T(K) = 1000 K

wnu(cm^{-1})	$w(-\Delta\omega)/N$	$w(+\Delta\omega)/N$
0.0	0.4372	0.4372
5.0	0.4392	0.4424
10.0	0.4444	0.4521
15.0	0.4524	0.4662
20.0	0.4631	0.4842
25.0	0.4763	0.5058
50.0	0.5726	0.6507
100.0	0.8494	1.0185
200.0	1.4315	1.7516
300.0	2.1897	2.3863
500.0	3.0461	3.3882
1000.0	5.4202	4.7610
1500.0	7.7315	4.9751
2000.0	9.7106	4.3831
2500.0	12.072	3.3667
3000.0	10.410	2.0039

References

Allard, N.F., Royer, A., Kielkopf, J.F., Feautrier, N.: 1999, *Phys. Rev. A* **60**, 1021

Allard, N.F., Allard, F., Hauschildt, P.H., Kielkopf, J.F., Machin, L.: 2003, Astron. Astrophys. **411**, L473

Baranger, M.: 1958, *Phys. Rev. A* **111**, 481

Beuc, R., Peach, G., Movre, M., Horvatić, B.: 2018, *Astron. and Astrophys. Trans.* **30**, 315

Burrows, A., Volobuyev, M.: 2003 Astrophys. J. **583**, 985

Kielkopf, J.F., Allard, N.F., Babb, J.: 2012, *EAS Publications Series* **58**, 75

Mullamphy, D.F.T., Peach, G., Venturi, V., Whittingham, I.B., Gibson, S.J.: 2007, *J. Phys. B: At. Mol. Opt. Phys.* **40**, 1141

Peach, G.: 1982, *Comment. At. Mol. Phys.* **11**, 101

Peach, G.: 2011, *Baltic Astron.* **20**, 516
Errata: headings 'Impact Theory — Baranger Theory' in tables 5-9 to be replaced by 'Baranger Theory — V d Waals Theory'

Peach, G., Whittingham, I.B.: 2009, *New Astron. Rev.* **53**, 227