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Electron detachment from alkali-metal negative ions by electron collisions

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Abstract. The Bethe–Born and Born–Ochkur approximations have been used to calculate the cross sections for electron detachment from the alkali metal negative ions Li^-, Na^-, K^-, Rb^- and Cs^-.

1. Introduction

Interest in reactions involving alkali metal negative ions has arisen from work on alkali metal vapours and gaseous plasmas. There is little information on the collisional detachment from alkali metal negative ions by electron impact, and the purpose of the present paper is to provide estimates of the cross sections. We use a simplified version of the Born–Ochkur approximation. This approach treats the incident and scattered electrons as plane waves but allows for distortion for the detached electron. This method has proved to be reliable in the case of the negative hydrogen ion (John and Williams 1973), their results were in good agreement with more elaborate calculations and experiment.

A discussion of the method is given in § 2 and the results in § 3.

2. A simplified version of the Born–Ochkur approximation

The cross section for the collisional ionization of an alkali metal negative ion is given by the alternative formulae

$$\left.\begin{aligned} Q_1(k_1^2) &= \frac{4}{\pi k_1^2}\int_0^{\epsilon_{\max}}\int_{k_1-k_3}^{k_1+k_3} K^{-3}|I(K,k_2^2)|^2\,\mathrm{d}K\,\mathrm{d}k_2^2 \\ &\qquad\qquad (\text{in units of } \pi a_0^2) \\ Q_2(k_1^2) &= \frac{8}{\pi k_1^2}\int_0^{\frac{1}{2}\epsilon_{\max}}\int_{k_1-k_3}^{k_1+k_3} K^{-3}|I(K,k_2^2)|^2\,\mathrm{d}K\,\mathrm{d}k_2^2 \end{aligned}\right\} \tag{1}$$

where $\boldsymbol{k}_1$, $\boldsymbol{k}_2$ and $\boldsymbol{k}_3$ are the momenta of the incident, detached and scattered electrons respectively, $\boldsymbol{K} = \boldsymbol{k}_3 - \boldsymbol{k}_1$, γ^2 is the attachment energy of the negative ion and $\epsilon_{\max} = k_1^2 - \gamma^2$. Q_1 and Q_2 give identical results for exact calculations (see Peterkop 1961). However, differences arise in the Born approximation for which $I(K, k^2)$ is given by

$$I(K,k^2) = \int \mathrm{e}^{\mathrm{i}Kz}\phi_{\gamma^2}^*\phi_{k^2}\,\mathrm{d}\tau \tag{2}$$

ϕ_{γ^2}, ϕ_{k^2} being the bound state and continuous state wavefunctions of the negative ion.

In the Bethe–Born approximation (2) is replaced by

$$|I(K, k^2)| = K \int z\phi_{\gamma^2}\phi_{k^2}\, \mathrm{d}\tau \tag{3}$$

so that

$$\int_{k_1-k_3}^{k_1+k_3} K^{-3}|I(K, k^2)|^2\, \mathrm{d}K = \frac{a(k^2)}{4\pi\alpha a_0^2(\gamma^2+k^2)} \ln\left|\frac{k_1+k_3}{k_1-k_3}\right| \tag{4}$$

$a(k^2)$ being the photoionization cross section for the reaction

$$A^- + h\nu \rightarrow A + e^-$$

α the fine structure constant and a_0 the Bohr radius. The photo-detachment cross section of alkali metal negative ions has been calculated (John 1972, John and Williams 1972) by the Bethe–Longmire formula

$$a(k^2) = \frac{32\pi\alpha}{3} a_0^2 \gamma N^2 \left[\frac{k}{\gamma^2+k^2}\right]^3 \left(\cos\eta_1^+ + \frac{\gamma(\gamma^2+3k^2)}{2k^3}\sin\eta_1^+\right)^2. \tag{5}$$

These cross sections are in satisfactory agreement with more elaborate calculations of Norcross and Moores (1972) for Li^- and Na^- and the Li^- measurements of Feldman (1972 private communication). The essential feature of the Bethe–Longmire method is that the wavefunction for the valence electron undergoing the transition is approximated by

$$P_{\gamma^2}(r) = \left[\frac{\gamma}{2\pi}\right]^{1/2} N \frac{e^{-\gamma r}}{r} \qquad \text{(bound state)}$$

$$P_{k^2}(r) = \left[\frac{3}{4\pi}\right]^{1/2} \frac{\cos\theta}{r} k^{-1/2} \left\{\frac{\sin(kr+\eta_1^+)}{kr} - \cos(kr+\eta_1^+)\right\} \qquad \text{(free state)} \tag{6}$$

N being a normalizing constant.

If we use the wavefunctions (6) to calculate $I(K, k^2)$ we get

$$\begin{aligned} |I(K, k^2)| &= \left(\frac{6\gamma}{k}\right)^{1/2} NK^{-1} \int_0^\infty \frac{e^{-\gamma r}}{r} \left(\frac{\sin Kr}{Kr} - \cos Kr\right) \left(\frac{\sin(kr+\eta_1^+)}{kr} - \cos(kr+\eta_1^+)\right) \mathrm{d}r \\ &= \left(\frac{6\gamma}{k}\right)^{1/2} NK^{-1}(P(K, k^2)\cos\eta_1^+ + Q(K, k^2)\sin\eta_1^+). \end{aligned} \tag{7}$$

Details of the derivation and explicit forms of P and Q are given in an appendix. The Bethe–Born version can be obtained by expanding P and Q in a series in K, neglecting terms of higher order than K^2:

$$\begin{aligned} P(K, k^2) &\simeq \frac{2K^2}{3} \frac{k^2}{(\gamma^2+k^2)^2} \\ Q(K, k^2) &\simeq \frac{\gamma K^2}{3k(\gamma^2+k^2)^2}(\gamma^2+3k^2) \end{aligned} \tag{8}$$

consistent with (4) and (5).

Exchange effects can be included in the Born approximation by the Ochkur correction (Ochkur 1964), the relevant Born–Ochkur expression for $|I(K, k^2)|^2$ is

$$|I(K, k^2)|^2 = 6\gamma N^2 K^{-2} k^{-1} \{P(K, k^2) \cos \eta_1^+ + Q(K, k^2) \sin \eta_1^+\}^2 \left(1 - \frac{K^2}{k_1^2} + \frac{K^4}{k_1^4}\right). \tag{9}$$

3. Discussion of results

We use (9) and (5) to calculate the Born–Ochkur and Bethe–Born versions of the detachment cross section, we find that $Q_2 \simeq 2Q_1$ at nearly all energies. From work on the detachment of H^-, we found the Born–Ochkur Q_2 gave the most accurate values and we expect the same to be true for the alkali metal negative ions. In the Bethe–Born approximation Q_1 was the most reliable form and is in agreement with the Born–Ockhur Q_2. We adopted the same data as was used in the photodetachment calculations, that is, the electron affinities of Weiss (1961, 1966) and the phases of Burke and Taylor (1969) for e–Li scattering, Karule and Peterkop (1965) for e–Na, e–K and e–Cs and Balling (1969) for e–Rb scattering. N^2 was calculated from the oscillator strength sum rule

$$\int_0^\infty a(k^2)\, dk^2 = 8\pi^2 \alpha a_0^2. \tag{10}$$

Our results are given in table 1, the cross sections of the negative ions in the various approximations, apart from Rb^-, show a similar pattern; for Rb^- the Bethe–Born and Born–Ochkur Q_2 differ by about 9 per cent at high energies.

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Appendix

The integrals arising in the Born approximation are of the form

$$J = \frac{-1}{2kK} \int_0^\infty e^{-\gamma r}(\sin Kr - Kr \cos Kr)\{\sin(kr+\eta) - kr \cos(kr+\eta)\}\, d(r^{-2}) \tag{A.1}$$

integrating by parts we can reduce J to integrals of the standard types:

$$\int_0^\infty r^{-1} e^{-\gamma r} \sin Kr \sin(kr+\eta)\, dr$$

$$\int_0^\infty r^n e^{-\gamma r} \begin{pmatrix} \sin Kr \\ \cos Kr \end{pmatrix} \begin{pmatrix} \sin(kr+\eta) \\ \cos(kr+\eta) \end{pmatrix} dr \qquad (n = 0, 1)$$

which can be evaluated by elementary methods, giving

$$J = P(K, k^2) \cos \eta + Q(K, k^2) \sin \eta \tag{A.2}$$

Table 1. The cross section for detachment of the alkali metal negatives by electron collisions (in units πa_0^2)

Lithium			
γ^2 (Ryd 13·6 eV) 0·0452			
N^2 1·839			
k_1^2 (eV)	Born–Ochkur Q_1	Born–Ochkur Q_2	Bethe–Born Q_1
3·3	198	353	479
6·1	154	305	359
11·5	106	213	237
27·8	59·3	118	124
55	35·1	70·1	72·7
109·4	20·3	40·5	41·2
136	16·9	33·8	34·7
190·4	12·8	25·5	26·2
299·2	8·7	17·4	17·8
408	6·7	13·4	13·7
489·6	5·7	11·4	11·7
571·2	5·0	10·0	10·2
652·8	4·5	9·0	9·1
734·4	4·0	8·0	8·2
816	3·7	7·4	7·5
897·6	3·4	6·8	6·9
979·2	3·2	6·3	6·4

	Sodium			Potassium			Caesium		
γ^2	0·0396			0·0344			0·0287		
N^2	2·550			1·176			1·314		
k_1^2 (eV)	Born–Ochkur Q_1	Born–Ochkur Q_2	Bethe–Born Q_1	Born–Ochkur Q_1	Born–Ochkur Q_2	Bethe–Born Q_1	Born–Ochkur Q_1	Born–Ochkur Q_2	Bethe–Born Q_1
3·6	306	—	—	265	—	—	573	—	—
3·67	—	—	803	—	—	566	—	—	1108
4·6	271	518	—	234	451	—	498	972	—
4·76	—	—	738	—	—	488	—	—	942
5·6	248	—	—	210	—	—	438	—	—
6·6	—	429	—	—	368	—	—	683	—
6·8	223	—	540	187	—	402	384	—	756
8·16	201	—	465	166	—	344	337	—	651
10·9	167	335	388	135	271	286	272	544	533
13·6	144	288	325	125	230	238	230	459	446
21·8	103	207	229	81	162	167	159	318	310
27·2	87·6	175	193	68·2	136	140	133	267	260
54·4	51·4	103	112	39·3	78·6	80·6	75·8	152	148
81·6	37·2	74·4	80·2	28·3	56·5	58·3	54·1	108	106
108·8	29·4	58·9	63·2	22·3	44·5	45·9	42·4	84·9	83·3
136	24·5	49·1	52·5	18·5	36·9	38·1	35·6	70·3	68·8
190·4	18·5	37·1	39·5	13·9	27·8	28·6	26·4	52·7	51·7
299·2	12·7	25·4	26·9	9·5	18·9	19·4	17·8	35·7	35·0
408	9·7	19·5	20·6	7·3	14·5	14·9	13·7	27·3	26·8
489·6	8·3	16·7	17·6	6·2	12·4	12·7	11·6	23·3	22·9
571·2	7·3	14·6	15·4	5·4	10·8	11·1	10·2	20·3	20·0
652·8	6·5	13·0	13·7	4·8	9·6	9·9	9·0	18·1	17·8
734·4	5·9	11·8	12·4	4·4	8·7	8·9	8·2	16·3	16·0
816	5·3	10·7	11·3	3·9	7·9	8·1	7·4	14·9	14·6
897·6	5·0	9·9	10·4	3·7	7·3	7·5	6·8	13·7	13·4
979·2	4·6	9·4	9·6	3·4	6·8	6·9	6·3	12·6	12·4

Rubidium			
γ^2 0·0309			
N^2 0·879			
k_1^2 (eV)	Born–Ochkur Q_1	Born–Ochkur Q_2	Bethe–Born Q_1
3·7	—	—	1295
3·8	805	1583	—
5·6	—	—	992
7·2	504	998	—
9·25	—	—	690
10·6	372	—	—
14	299	596	506
20·8	—	433	374
27·2	174	—	301
27·6	—	343	298
54·4	97·4	195	171
81·6	69·0	138	122
136	44·5	88·9	79·4
108·8	53·9	108	95·9
190·4	33·2	66·4	59·5
299·2	22·4	44·8	40·3
408	17·0	34·0	30·8
489·6	14·5	29·0	26·3
571·2	12·7	25·3	22·9
652·8	11·2	22·4	20·4
734·4	10·1	20·2	18·4
816	9·2	18·4	16·8
897·6	8·5	17·0	15·4
979·2	7·8	15·6	14·3

where

$$P(K,k^2) = \left(\frac{\gamma^2+k^2+K^2}{8kK}\right)\ln\left(\frac{\gamma^2+(k+K)^2}{\gamma^2+(k-K)^2}\right)-\frac{1}{2}$$
$$Q(K,k^2) = \left(\frac{\gamma^2+k^2+K^2}{4kK}\right)\left\{\tan^{-1}\left(\frac{k+K}{\gamma}\right)-\tan^{-1}\left(\frac{k-K}{\gamma}\right)\right\}-\frac{\gamma}{2k}. \tag{A.2}$$

References

Balling L C 1969 *Phys. Rev.* **179** 78–94

Burke P G and Taylor J 1969 *J. Phys.* B: *Atom. molec. Phys.* **2** 869–77

Karule E M 1965 *JILA Inf. Center Rept.* No. 3, University of Colorado, Boulder, Colorado (trans. *Atomic Collision III* ed Y Ia Veldre, Latvia Acad. Sc. Riga 1965)

Karule E M and Peterkop R K 1965 *JILA Inf. Center Rept.* No. 3, University of Colorado, Boulder, Colorado (trans. *Atomic Collisions III* ed Y Ia Veldre, Latvian Acad. Sc. Riga 1965)

Karule E M 1972 *J. Phys.* B: *Atom. molec. Phys.* **5** 2051–60

John T L 1972 *J. Phys.* B: *Atom. molec. Phys.* **5** L121–3

John T L and Williams A R 1972 *J. Phys.* B: *Atom. molec. Phys.* **5** 1662–75

John T L and Williams B 1973 *Phys. Lett.* (Netherlands) **43A** 463–4

Norcross D W and Moores D L 1972 *Atomic Physics III*, Proc. of 3rd Int. Conf. on Atomic Physics, Boulder 1972 (New York: Plenum)

Ochkur V I 1964 *Sov. Phys.–JETP* **18** 503–8

Peterkop R 1961 *Proc. Phys. Soc.* **77** 1220–2

—— 1962 *Sov. Phys.–JETP* **14** 1377–8

Weiss A W 1961 *Phys. Rev.* **122** 1826–36

—— 1968 *Phys. Rev.* **166** 70–4