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Revised high energy behavior of the Deutsch-Märk (DM) formula for the calculation of electron impact ionization cross sections of atoms

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Abstract

We modified the Deutsch-Märk (DM) formula for the calculation of single atomic ionization cross sections by replacing the previously used Gryzinsky-type energy dependence by a "scaled" ln(*E*)/*E* energy dependence. This modified energy dependence yields, in the limit of high impact energies, the well-established Born–Bethe ln(*E*)/*E* energy dependence, while reproducing, at lower impact energies, the DM cross section function. The revised DM formula, whose energy dependence has been determined from a fitting procedure using reliable, measured ionization cross sections for the atoms H, He, C, Ne, Mg, Al, and Ag, was subsequently used to calculate as an example ionization cross sections for the atoms O, F, P, Ar, Ge, Kr, and Xe and excellent to very good agreement was found between the calculated and the measured cross sections for these atoms over a wide range of impact energies.

Keywords: Electron impact ionization; Cross sections; Atoms

1. Introduction

Significant progress has been made in the past 15 years in the measurement and calculation of electron impact ionization cross sections of atoms, molecules, free radicals, and clusters (see e.g., [1–7] and references therein to earlier publications). Among the first semi-rigorous methods to calculate electron-impact ionization cross sections for atoms were the Deutsch-Märk (DM) formalism [3,8] and the binary-encounter-dipole (BED) method of Kim and Rudd [5]. While both methods can be applied in principle to any atom in the periodic table, BED calculations are available only for H, the noble gases, and the halogen atoms Cl, J, and Br, whereas DM calculations were carried out for all atoms for which experimentally determined ionization cross sections are available (H, He, Li, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Ti, V, Fe, Ni, Cu, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Ag, In, Sn, Sb, Te, I, Xe, Cs, Ba, Yb, Hg, Pb, Bi, and U) [9]. More recently, a fully quantum mechanical theory, the convergent close coupling (CCC) method [7,10] has been applied to the calculation of atomic electron impact ionization cross sections. However, this method is computationally intensive and has only been applied to atoms with one or two electrons in the valence shell. In the limit of high impact energies E, both the BED method and the CCC theory yield cross section shapes that have the expected ln(*E*)/*E* energy dependence. In contrast, the DM formula uses a Gryzinski-type energy dependence, which does not reproduce the quantum mechanically "correct" ln(*E*)/*E* behavior at high impact energies. We note in this context, that the DM formalism was originally developed primarily to provide a reliable description of atomic ionization cross sections in the low-energy regime from threshold to about 100 eV, which is of particular interest in low-temperature plasma environments and this is where the strength of the DM formula lies.

In an effort to extend the range of validity of the DM formalism to higher impact energies, we derived a modified DM formula where we replaced the Gryzinsky-type energy dependence by a "scaled" ln(*E*)/*E* energy dependence,

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which, in the limit of high impact energies, reproduces the ln(*E*)/*E* dependence and which, at lower impact energies, yields the previously calculated DM cross sections. The revised DM formula, whose high-energy dependence has been determined from a fitting procedure using reliable, measured ionization cross sections for the atoms H, He, C, Ne, Mg, Al, and Ag, was subsequently used to calculate as an example ionization cross sections for the atoms O, F, P, Ar, Ge, Kr, and Xe and excellent to very good agreement was found between the calculated and the measured cross sections for these atoms.

2. Theoretical background

In the original concept, the DM formalism [8] expressed the total single electron-impact ionization cross section σ of an atom as

$$\sigma(u) = \sum_{n,l} g_{nl}\, \pi\, r_{nl}^2\, \xi_{nl}\, f(u) \tag{1}$$

where r_{nl} is the radius of maximum radial density of the atomic subshell characterized by quantum numbers n and l (as listed in column 1 in the tables of Desclaux [11]) and ξ_{nl} is the number of electrons in that subshell. The sum extends over all atomic sub-shells labelled by n and l. The factors g_{nl} are weighting factors which were originally determined from a fitting procedure [3,8,9] using reliable experimental cross section data for the rare gases and uranium. The energy dependence of the cross section was contained in the function $f(u)$ which, following the concept of Gryzinsky [12], had the form

$$f(u) = d\frac{1}{u}\left(\frac{u-1}{u+1}\right)^a \left\{b + c\left(1-\frac{1}{2u}\right)\ln(2.7+(u-1)^{1/2})\right\} \tag{2}$$

where $u = E/E_{nl}$. Here E refers to the incident energy of the electrons and E_{nl} is the ionization energy in the (nl) subshell. The constants a, b, c, d have different values for s-, p-, d-, and f-electrons as one expects on the basis of the different angular shapes of atomic s-, p-, d-, and f-orbitals. Values of these constants as well as all other parameters relevant to the application of the DM formula can be found in the topical review by Deutsch et al. [3]to which we refer the reader for further details of the DM formalism. We note that the energy dependence of Eq. (2), in the limit of high impact energies, does not yield the ln(*E*)/*E* or ln(*u*)/*u* energy dependence that the Born–Bethe theory predicts and that has been verified experimentally.

In an effort to extend the range of validity of the DM formalism from the low-energy regime (ionization threshold to typically 200 eV), for which the DM method was originally developed to higher impact energies, we introduce a modified DM formula with a revised energy dependence that has a high-energy form similar to that of the Bethe formula [13] and has the following explicit form

$$\sigma(u) = \sum_{n,l} g_{nl}\, \pi\, r_{nl}^2\, \xi_{nl}\, b_{nl}^{(q)}(u) \left[\frac{\ln(c_{nl}\, u)}{u}\right] \tag{3}$$

While the coefficients b_{nl} in the Bethe high-energy formula do not depend on the energy, we introduce energy-dependent quantities $b_{nl}^{(q)}(u)$ in an effort to merge the high-energy Born–Bethe region of the ionization cross sections with the more accurate DM representations of the cross sections in the regime of low impact energies (where the Born–Bethe formula is known to yield cross sections that significantly exceed experimental values [13,14]). The energy-dependent function $b_{nl}^{(q)}(u)$ has the explicit form

$$b_{nl}^{(q)}(u) = \frac{(A_1 - A_2)}{[1 + (u/A_3)^p]} + A_2 \tag{4}$$

and the four quantities A_1, A_2, A_3, and p are constants that have to be determined (in conjunction with the constant c_{nl}) from reliable measured cross sections for the various values of n and l. The superscript "q" refers to the number of electrons in the (nl) subshell and allows the possibility to use slightly different functions $b_{nl}^{(q)}(u)$ depending on the number of electrons in a given (nl) subshell. The function $b_{nl}^{(q)}(u)$ ensures that, in the low-energy regime, the cross sections calculated from Eq. (3) reproduce the cross sections derived from Eq. (1), which were found to agree well with available experimental data [9]. On the other hand, at high impact energies (as u approaches infinity), the first term in Eq. (4) goes to zero and $b_{nl}^{(q)}(u)$ becomes a constant, which, in turn, ensures the "correct" high-energy behavior of the cross section as predicted by the Born–Bethe theory [13]. The constant c_{nl} in Eq. (3) was found to be close to one except for d-electrons (see below).

In order to apply the revised DM formula of Eq. (3), we need to determine the four constants A_1, A_2, A_3, and p that characterize the function $b_{nl}^{(q)}(u)$ for the various values of n and l as well as the subshell occupancy q and the constant c_{nl}. This is conceptually similar to what was done in order to determine the four constants a, b, c, and d in the previously used energy-dependent function $f(u)$, which were found to depend only on the quantum number l. We used the reliable cross sections for the single ionization of the atoms H, He, C, Ne, Mg, Al, and Ag [1,15–17] to obtain values for the above parameters for the various values of n and l. The results of this fitting procedure are summarized in Table 1 and the measured single ionization cross sections of these "benchmark" atoms along with the fitted curves are shown in Fig. 1.

3. Results and discussion

Using the revised DM formula of Eq. (3) together with the parameters summarized in Table 1, we now calculated the single ionization cross sections for the atoms O, F, P,

Table 1
Summary of parameters A_1, A_2, A_3, and p that characterize the energy-dependent function $b_{nl}^{(q)}(u)$ of Eq. (4)

Function $b_{nl}^{(q)}(u)$	A_1	A_2	A_3	p	c_{nl}
$b_{ns}^{(1)}(u)$, $n = 1, 2, 3, \ldots$	0.31	0.87	2.32	1.94	1.00
$b_{ns}^{(2)}(u)$, $n = 1, 2$	0.23	0.86	3.67	2.08	1.01
$b_{np}^{(q)}(u)$, $n = 2$; $q = 1,2$	0.33	0.88	2.38	1.98	0.99
$b_{np}^{(q)}(u)$, $n = 2$; $q = 3$–6	−0.15	1.17	4.05	1.31	1.01
$b_{ns}^{(2)}(u)$, $n = 3, 4, 5, \ldots$	1.04	−0.08	31.20	0.34	0.96
$b_{np}^{(q)}(u)$, $n = 3, 4, 5, \ldots$; $q = 1$–6	0.59	1.06	10.34	1.83	0.93
$b_{nd}^{(q)}(u)$, $n = 3, 4, 5, 6$; $q = 1$–10	0.44	1.55	4.38	1.87	1.42

These parameters were determined from reliable measured cross sections for the single ionization of the atoms H, He, C, Ne, Mg, Al, and Ag. Also included are the values of the constant c_{nl}.

Ar, Ge, Kr, and Xe, where reliable experimental data have also been reported [1,15,16,18]. The results are summarized in Fig. 2. In oxygen, we compare the calculated cross sections with the experimental data of Ref. [16] and Ref. [18] and find good agreement with both data sets over the entire energy range except perhaps near the maximum, where the data of Ref. [18] lie somewhat above the data of Ref. [16] and the present calculation. In the case of F, P, and Ge, the only experimental data available are those of Freund et al. [1] up to an impact energy of 200 eV. In that energy range, our calculated cross section reproduces the measured data quite well with only minor discrepancies near the maximum in the F and P cross sections, which are, however, well within the stated experimental uncertainty.

The single ionization cross sections of the rare gases are perhaps the best-known atomic ionization cross sections with a level of agreement between the most reliable measurements of better than 5% [15]. Because of this high level of accuracy, the cross sections for He and Ne were included in the set of reliable cross section data that was used to determine the fitting parameters (see above). In turn, we can now use the well-known single ionization cross sections of Ar, Kr, and Xe to test the reliability of our revised DM cross section formula. The results are also shown in Fig. 2, where we use the most accurate data of Stebbings and co-workers [15] for comparison with our calculation. The agreement between measured and calculated cross section is excellent in the case of Kr and Xe, where the revised DM formula even shows a hint of the structure in the cross section near

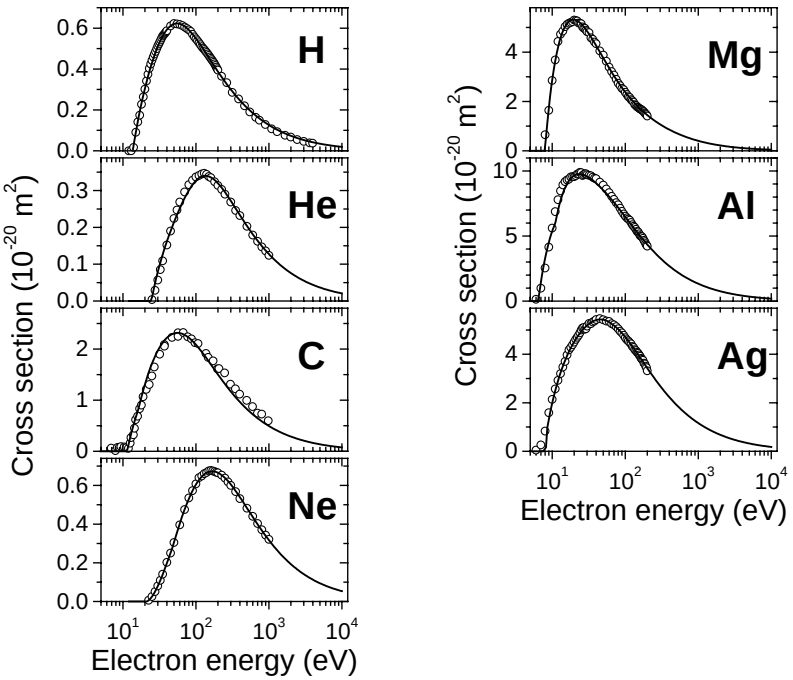

Fig. 1. Comparison between presently calculated (DM) and measured electron impact single ionization cross sections for H, He, C, Ne, Mg, Al and Ag. The experimental data are from Ref. [1] (Mg, Al, Ag), Ref. [15] (He, Ne), Ref. [16] (C) and Ref. [17] (H). The comparison between these measured and calculated cross sections were used to determine the fitting parameters that are required for the DM formula of Eq. (3) (see text for further details).

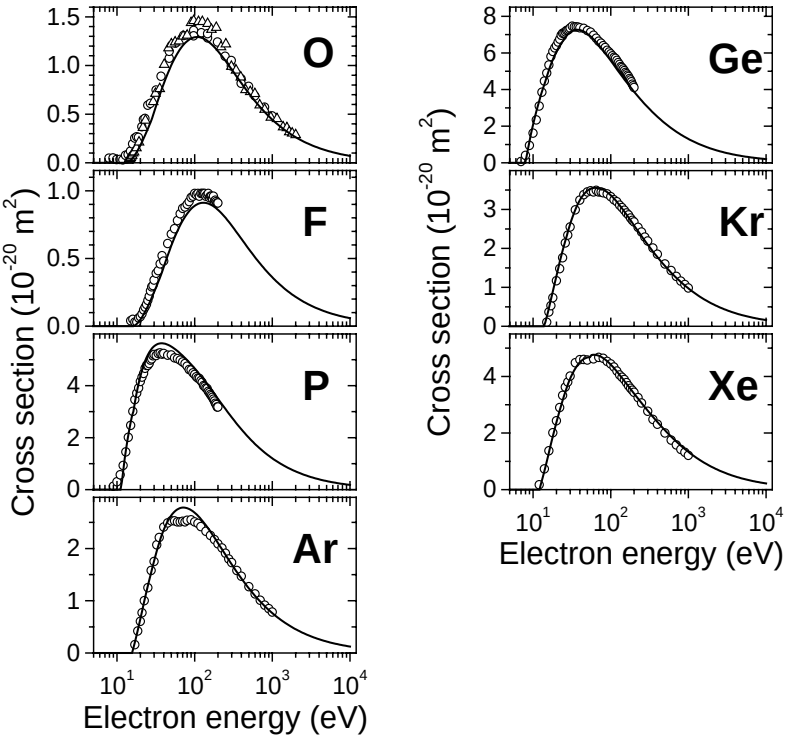

Fig. 2. Comparison between presently calculated and measured electron impact single ionization cross sections for O, F, P, Ar, Ge, Kr, and Xe. The experimental data are from Ref. [1] (F, P, Ge) and Ref. [15] (Ar, Kr, Xe) two sets of oxygen data are shown, Ref. [16] (circles) and Ref. [18] (triangles).

its maximum. The level of agreement in the case of Ar is not quite as impressive as the maximum in the DM cross section lies slightly above the maximum in the measured curve and it does not show any indication of the well-known structure near the maximum of the Ar single ionization cross section. Nevertheless, the overall agreement for Ar is still very good.

4. Summary

In an effort to improve the accuracy of the Deutsch-Märk (DM) formula for the calculation of single atomic ionization cross sections, which was originally developed for the low-energy region below 100 eV, into the regime of higher impact energies, we replaced the previously used Gryzinsky-type energy dependence by a "scaled" $\ln(E)/E$ energy dependence, which yields the well-established Born–Bethe $\ln(E)/E$ energy dependence at high impact energies, while reproducing, at lower impact energies, the calculated DM cross section function. The revised DM formula, whose high-energy dependence has been determined from a fitting procedure using reliable, measured ionization cross sections for the atoms H, He, C, Ne, Mg, Al, and Ag, was subsequently used to calculate ionization cross sections for the atoms O, F, P, Ar, Ge, Kr, and Xe and excellent to very good agreement was found between the calculated and the measured cross sections for these atoms over a wide range of impact energies.

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References

[1] R.S. Freund, R.C. Wetzel, R.J. Shul, T.R. Hayes, Phys. Rev. A 41 (1990) 3575.
[2] R. Basner, M. Schmidt, K. Becker, J. Chem. Phys. 118 (2003) 2153.
[3] H. Deutsch, K. Becker, S. Matt, T.D. Märk, Int. J. Mass Spectrom. Ion Proc. 197 (2000) 37.
[4] S. Matt, P. Scheier, T.D. Märk, K. Becker, in: K. Becker (Ed.), Novel Aspects of Electron-Molecule Collisions, World Scientific, Singapore, 1998, p. 1.
[5] Y.K. Kim, M.E. Rudd, Phys. Rev. A 50 (1994) 3954.
[6] W.M. Huo, V. Tarnovsky, K. Becker, Chem. Phys. Lett. 358 (2002) 328.
[7] P.L. Bartlett, A.T. Stelbovics, Phys. Rev. A 66 (2002) 012707.
[8] H. Deutsch, T.D. Märk, Int. J. Mass Spectrom. Ion Proc. 79 (1987) R1.
[9] D. Margreiter, H. Deutsch, T.D. Märk, Int. J. Mass Spectrom. Ion Proc. 139 (1994) 127.

[10] I. Bray, A.T. Stelbovics, Adv. At. Mol. Phys. 35 (1995) 209.
[11] J.P. Desclaux, Atom. Data Nucl. Data Tables 12 (1973) 325.
[12] M. Gryzinski, Phys. Rev. A 138 (1965) 305.
[13] H. Bethe, Ann. Phys. (Leipzig) 5 (1930) 325.
[14] See e.g., C.J. Powell, in: T.D. Märk, G.H. Dunn (Eds.), Electron Impact Ionization, Springer, Vienna, 1985.
[15] R. Rejoub, B.G. Lindsay, R.F. Stebbings, Phys. Rev. A65 (2002) 042713.
[16] E. Brook, M.F.A. Harrison, A.C.H. Smith, J. Phys. B 11 (1978) 3115.
[17] M.B. Shah, D.S. Elliot, H.B. Gilbody, J. Phys. B20 (1987) 3501.
[18] W.R. Thompson, M.B. Shah, H.B. Gilbody, J. Phys. B28 (1995) 1321.