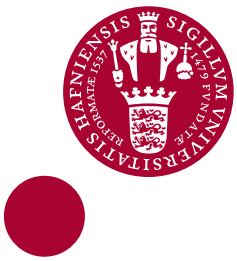

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# Mean excitation energies of singly charged atomic anions

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***Abstract***

We present hitherto unknown mean excitation energies of singly charges atomic anions wit Z≤ 18. Most are calculated using the Random-phase Approximation and large basis sets but some are estimated from the relationship that we have found between atomic mean excitation energies of atoms and ions with same nuclear charge but different number of electrons.

***Keywords****: electronic structure, excited states, mean excitation energies, atomic anions, stopping power, plasma physics*

## *1. Introduction*

Negative ions are abundant in interstellar space[1], in atmospheres[2], and in plasmas[3]. The basic physical properties of negative ions are thus needed to explain and understand the nature of the complicated chemical processes that determine the physical conditions both inside and outside of our planet. Even though laboratory experiments on negative ions are inherently difficult due to interactions with the surroundings, ion trapping[4] and new cryogenic ion-storage ring techniques now allow the study of ions such as $S^-$ for minutes and hours[5], and will be providing much needed information on properties of anions. Also, theoretical methods may provide some information on some of the central physical quantities that are required in the modelling of matter in interstellar space, atmospheres, and plasmas, and among those is material constants related to the slowing down of heavy fast particles penetrating materials, *i.e.* stopping power. In 1930 Bethe formulated the quantum theory for stopping power[6] showing that the most essential material constant determining the bulk of the stopping for fast projectiles is the mean excitation energy[7], $I_0$, of the target.

Even though the literature on mean excitation energies is quite extensive, little has been reported for the mean excitation energy of negative ions. Here we report mean excitation energies for singly charged anions of the first, second, and third row atoms, *i.e.* the same atoms for which we recently reported mean excitation energies for all neutral and positively charged atoms[8]. Most of the mean excitation energies are calculated using contemporary electronic structure theory and

the rest are estimated based on the relationship we find between mean excitation energies of anions, neutral and cations with the same nuclear charge.

## *2. Theory*

When a heavy, fast projectile collides with a target, it is slowed down due to the interaction with the electrons of the target. For sufficiently fast projectiles, *e.g.* MeV protons, the slowing down process is primarily caused by exciting the electrons of the target. The more difficult it is to excite the electrons of the target, the more the projectile is slowed down. Bohr[9] was the first to describe the stopping of fast projectiles by target electrons, and the quantum theory for it was formulated by Bethe[6].

In atomic units, Bethe's[6] expression for the stopping cross section of a target, S(v), for a projectile with velocity v is

$$S(v) = \frac{4\pi Z_1^2 Z_2}{v^2} ln \frac{2v^2}{I_0} \quad (1)$$

Here, $Z_1$ and $Z_2$ are the charge of the projectile and the number of electrons of the target, respectively. This is the simplest approximation to stopping power and we are disregarding corrections to the Bethe equation as shell corrections and contributions proportional to higher powers of $Z_1$, most noticeable Barkas[10] and Bloch[11] corrections. However, Eq. (1) will give the leading contributions to the slowing down of fast, energetic particles. Thus, in this approximation, the stopping cross section of a target is determined by only one material constant, the mean excitation energy of the target

$$I_0 = \exp(\frac{\sum_n f_{n0} ln E_{n0}}{\sum_n f_{n0}}) \quad (2)$$

Here $E_{n0} = E_n - E_0$ is the excitation energy of the system between the ground state $< 0 |$ and an excited state $< n |$ and

$$f_{n0} = \frac{2}{3} < 0|\boldsymbol{r}|n > \cdot < n|\boldsymbol{r}|0 > E_{n0} \quad (3)$$

is the corresponding dipole oscillator strength in the dipole length formulation.

The summations in Eq. (2) extend over all excited states, bound as well as continuum. In principle there should have been a summation over the discrete, bound states and integration over the continuum states. However, in a finite basis set calculation one obtains a finite number of pseudo-states placed in the continuum and we use these states to calculate the continuum contributions to the mean excitation energy. We have shown[12] that this stick spectrum representation gives a good representation of the continuum contributions to the dipole oscillator sum rule, provided large and flexible basis sets are used and all states are included in the sum over states expressions for sum rules as the ones in Eq. (2).

Using the operator identity

$$[\boldsymbol{r}, H] = i\boldsymbol{p} \quad (4)$$

for one or both dipole operators in Eq. (3) we obtain the mixed and the dipole velocity formulations, respectively, for the dipole oscillator strength. In an exact theory the three formulations give the same

results for $f_{n0}$. However, this is also the case in the Random-Phase Approximation (RPA) when using a complete basis set[13].

Moreover, we know that the sum of the oscillator strengths in all three formulations in an exact theory and in RPA must fulfill the Thomas-Reiche-Kuhn (TRK) sum rule[14]

$$\sum_n f_{n0} = n \qquad (5)$$

where n is the number of electrons in the system.

Thus, the fulfillment of the TRK sum rule in the length, mixed and velocity formulation is a necessary condition for basis set completeness of an RPA calculation, a criterion we shall apply to test the reliability of our calculations.

## *3. **Computational details***

The mean excitation energies were obtained by explicitly summing over the excitation energies and corresponding oscillator strengths of all states obtained for the given anion in the employed one-electron basis set according to Eq. (2). The calculations of the excitation energies and oscillator strengths were carried out at the level of time-dependent Hartree-Fock theory, which is also known as Random-phase Approximation, using the Dalton program package[15]. For the calculations on anions with an open shell configuration the MCSCF module of DALTON was employed to generate the correct one configuration wavefunctions.

A preliminary study of the basis set dependence of the mean excitation energies of the anions showed that acceptable accuracy of the calculation required an addition of an extra set of diffuse functions compared to our previous calculations on the neutral atoms and cations[8]. Therefore, we did not employ the aug-cc-pCVXZ (X=Q,5) basis sets as in our previous studies,[8,16,17,18] but instead the d-aug-cc-pCVXZ ( X= Q,5) basis sets. For Li we thus employed the fully uncontracted d-aug-cc-pCVQZ basis set, for B, C, N, O, and F the d-aug-cc-pCV5Z basis set and for Na, Al, Si, P, S, and Cl the fully uncontracted d-aug-cc-pCV5Z basis set. With these basis sets the Thomas-Reiche-Kuhn sum rule[14] in Eq. ( 5) was fulfilled to within 0.25% in the length and velocity representations and even better in the mixed representation. The differences between the mean excitation energies in the three representations were in most cases less than 0.1 eV. Thus, only the results in the length representation are presented.

The Random-phase Approximation includes electron correlation to first order in the Hartree-Fock fluctuation potential and, as was discussed recently[8,18], this provides a sufficiently high level of electron correlation to calculate mean excitation energies to good enough accuracy for experimental purposes. We estimate that error bar on the calculated mean excitation energies will be of the order of 1-2 eV, the main cause of which will be additional electron correlation effects as the remaining basis set effects on the calculated $I_0$'s is smaller than 0.1 eV. Thus, the mean excitation energies reported here represent the RPA values to the quoted decimal places.

Some of the atoms in the second and third row have rather large estimated negative electron affinity: He( -0.52 eV[19]), Be( -0.52 eV[19]), Ne( -1.2 eV[19]), Mg( -0.415 eV[19]), and Ar( -1.0 eV[19]). For the anions of those atoms our finite basis set RPA calculations lead to erratic results for the sum rules, for instance containing oscillator strengths of the same irreducible representation as the orbital in which the extra electron was placed. They are therefore not included in this study. An exception is nitrogen, whose electron affinity is also negative but very close to zero (-0.000726 eV[19]). In this case we could obtain a meaningful RPA results also for $N^-$.

## *4. **Results***

Using the method described in the preceding section we have calculated the mean excitation energies for the singly charged anions listed in Table 1. We also list the parameters that were recently[8] used to analyze the cations of the same series of atoms. The parameters $Z_{\text{eff}}$ and S are defined through the relations

$$I_0 = Z_{\text{eff}}^2 \, I_0(\text{H}) \tag{6}$$

with $Z_{\text{eff}}$ being

$$Z_{\text{eff}} = Z - S \tag{7}$$

where $I_0$ is the calculated mean excitation energy, $I_0$(H) = 14.990 eV is the exact mean excitation energy of hydrogen[20] and Z is the nuclear charge of the atom or ion. The S parameter defined in Eq. (7) resembles a screening parameter but cannot meaningfully be so in all cases[8]. In the next section we will analyze the calculated mean excitation energies in terms of $Z_{\text{eff}}$ and S.

Table 1 contains results for all the singly charged negative ions for which were able to perform the RPA calculation described above.

Table 1. Mean excitation energies (in eV) for singly charged first, second and third row anions.

| Ion | $I_0$(eV) | $Z_{\text{eff}}$[b] | S[b] | $\Delta S$[c,d] | EA(eV)[e] | $I_0/Z$ |
|---|---|---|---|---|---|---|
| $H^-$ | 6.7[a] | 0.67 | 0.33 | | 0.75 | 6.7 |
| $Li^-$ | 13.5 | 0.95 | 2.05 | 0.27(0.34) | 0.62 | 4.5 |
| $B^-$ | 31.3 | 1.45 | 3.55 | 0.35(0.45) | 0.28 | 6.3 |
| $C^-$ | 44.9 | 1.73 | 4.27 | 0.40(0.48) | 1.26 | 7.5 |
| $N^-$ | 57.5 | 1.96 | 5.04 | 0.40(0.50) | 0 | 8.2 |
| $O^-$ | 73.5 | 2.21 | 5.79 | 0.42(0.51) | 1.46 | 9.2 |
| $F^-$ | 91.2 | 2.47 | 6.53 | 0.44(0.52) | 3.40 | 10.1 |
| $Na^-$ | 82.8 | 2.35 | 8.65 | 0.43(0.57) | 0.55 | 7.5 |
| $Al^-$ | 95.4 | 2.52 | 10.48 | 0.46(0.58) | 0.43 | 7.3 |
| $Si^-$ | 108.6 | 2.69 | 11.31 | 0.51(0.59) | 1.39 | 7.8 |
| $P^-$ | 119.3 | 2.82 | 12.18 | 0.53 | 0.75 | 8.0 |
| $S^-$ | 131.9 | 2.97 | 13.03 | 0.55 | 2.08 | 8.3 |
| $Cl^-$ | 145.6 | 3.12 | 13.88 | 0.57 | 3.61 | 8.6 |

[a] The mean excitation energy for $H^-$ is calculated in the same basis set as the rest of the negative ions. However, using the more extended basis set 13p17s+1-1-12 of Ref. 12 we find that $I_0(H^-)$ = 6.6483 eV.

[b] Defined in Eqs. (6) and (7).

[c] $\Delta S = S(X) - S(Y^-)$ where X and $Y^-$ are isoelectronic elements, *e.g.* X being F and $Y^-$ being $O^-$. The results for neutral atoms are taken from Tables 1-17 in Ref. 8.

[d] The number in parenthesis is the value ($D_N$) for $\Delta S$ in the isoelectronic series with the same number of electrons, see Table 19 in reference in Ref. 8.

[e] The electron affinity of the neutral atoms, see Ref. 21.

## *5. Discussion*

To the authors' knowledge there are no previous calculations or measurements of mean excitation energies for negative atomic ions available in the literature to which we may compare our calculated values. Thus, instead we have tried to see if some of the knowledge of the systematics of mean excitation energies of atoms and their positive ions also holds for the anions. To this end we have analyzed the mean excitation energies of the negative ions in terms of the parameters $Z_{eff}$ and S defined in Eqs. (6) and (7). We found recently[8] that the change in S with Z in an isoelectronic series was proportional to the Z for the atom or cation. We also saw that the proportionality constant increases slightly with the number of electrons in the isoelectronic series. This proportionality constant is given in parenthesis in column 5 of Table 1. As this constant is rather different from the ΔS value for the anion in the same column the quadratic dependence on Z that resulted from the constancy of ΔS for cations in an isoelectronic series cannot be extended to the anion in the same isoelectronic series. This is perhaps not as surprising as we found[8] that also for the neutral atom and the singly excited cation this relation did not hold so well. Thus, the quadratic dependence on Z for an isoelectronic series is restricted to positive ions with charges larger than 1.

The electron affinity of an atom describes how well an atom may attract an electron and perhaps this ability could also be related the magnitude of mean excitation energy of the atom. However, Table 1 shows that there is no correlation between these two atomic properties, the reason probably being that the electron affinity basically is a ground state property whereas $I_0$ is primarily determined by its continuum contributions[12,22].

In the last column of Table 1 we have illustrated how the mean excitation energies of the anions are fulfilling the Bloch[23] expression

$$I_0 = CZ \qquad (8)$$

where C is constant of the order 10 eV. This relation that holds rather well for small atoms in their natural phase[24], even though Eq. (8) was originally derived for heavy atoms. However, not unexpectedly Eq. (8) does not hold for the gas phase anions in Table 1 as they cannot be described by the Thomas-Fermi[25,26] theory that is the basis for the simple relationship in Eq. (8).

The Z-dependence of $I_0$ for neutral atoms shows periodic variations reflecting the shell structure of the atoms[8,27,28,29]. The mean excitation energies increase with Z within a shell but the last value in a shell tends to be larger than the first value (alkali atom) in next shell. As we can see from Table 1 this trend also holds for the mean excitation energies of the negative ions.

Another way of illustrating the relationship between the mean excitation energies of the negative and positive ions is provided by Fig. 1 and Table 2 where we have plotted and listed, respectively, the mean excitation energies of the negative as well as of the neutral and two first positive ions[8] for all atoms for which the four mean excitation energies are available.

Table 2. Comparison of mean excitation energies $I_0$ (in eV) of atoms (X) with varying charge (q).

| Atom (X) | q = -1 | q = 0[a] | q = 1[a] | q = 2[a] | $I_0(X^-)/I_0(X)$ | $I_0(X)/I_0(X^+)$ | $I_0(X^+)/I_0(X^{2+})$ | $I_0(X)$ from Bragg´s rule[b] | $\Delta I_0$[c] |
|---|---|---|---|---|---|---|---|---|---|
| Li | 13.5 | 33.1 | 108.3 | 134.2 | 0.40 | 0.31 | 0.80 | 27.1 | 6.0 |
| B | 31.3 | 52.6 | 82.3 | 136.9 | 0.60 | 0.64 | 0.60 | 46.1 | 6.5 |
| C | 44.9 | 65.9 | 92.6 | 134.8 | 0.68 | 0.71 | 0.69 | 60.7 | 5.2 |
| N | 57.5 | 81.6 | 107.4 | 142.4 | 0.71 | 0.76 | 0.75 | 75.2 | 6.4 |
| O | 73.5 | 97.9 | 125.2 | 157.2 | 0.75 | 0.78 | 0.80 | 92.8 | 5.1 |
| F | 91.2 | 116.5 | 144.0 | 176.4 | 0.78 | 0.81 | 0.82 | 111.7 | 4.8 |
| Na | 82.8 | 125.7 | 189.2 | 220.4 | 0.65 | 0.66 | 0.86 | 120.6 | 5.1 |
| Al | 95.4 | 132.2 | 172.7 | 225.8 | 0.72 | 0.77 | 0.76 | 125.5 | 6.7 |
| Si | 108.6 | 140.8 | 177.2 | 221.2 | 0.77 | 0.79 | 0.80 | 136.3 | 4.5 |
| P | 119.3 | 151.6 | 185.3 | 225.2 | 0.79 | 0.79 | 0.82 | 146.5 | 5.1 |
| S | 131.9 | 162.4 | 195.7 | 232.8 | 0.81 | 0.81 | 0.84 | 158.7 | 4.3 |
| Cl | 145.6 | 174.9 | 206.8 | 242.9 | 0.83 | 0.84 | 0.85 | 171.7 | 3.2 |

[a] From Tables 1-17 in Ref. 8.

[b] See the text following Eq. (9).

[c] $\Delta I_0$ is the difference between the RPA value for $I_0$ in column 3 and the value computed using Bragg's rule in column 9.

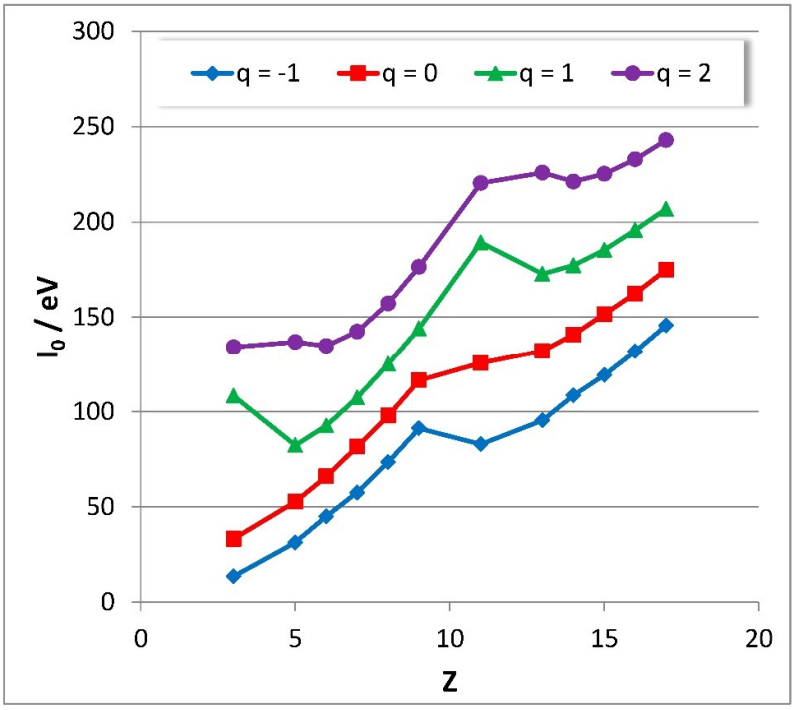


Figure 1. The mean excitation energies of atoms and three ions (in eV) as a function of nuclear charge.

As can be seen from both Fig. 1 and the ratios in Table 2 the mean excitation energy of any atomic ion is a decreasing function of the number of electrons in the ion. Furthermore, for most atoms $I_0$ decreases by a nearly constant factor when the number of electrons is decreased by 1 and this factor does not vary much from atom to atom. The factor is of the order ¾. This thus provides a simple way of estimating the mean excitation energy of an atomic ion if the mean excitation energy is known of the atom or one of the ions with the same nuclear charge.

It is, however, evident from Table 2 and Fig. 1 that this simple rule-of-thumb does not hold for all atoms, Li and to a certain extent also Na being the most noticeable exceptions. Also, the "constant" does vary both with the number of electrons in the ion and with the atomic number of the atom. In fact, it increases a bit with both parameters. If we disregard the Li-series we find ratios between neighboring ions vary between 0.60 and 0.85.

Another way of estimating mean excitation energies of one ion from that of other ions involves the use a variant of Bragg's rule[30]. This is also illustrated in Table 2.

Bragg's rule states that a good approximation to the stopping cross section of a sample may be obtained as a weighted sum of the stopping cross sections of the individual fragments of the sample. This implies that if the stopping cross sections are approximated by the expressions in Eq. (1) then Bragg's rule for mean excitation energies implies that

$$lnI_0 = \frac{1}{n}\sum_i w_i \, lnI_{0i} \tag{9}$$

where $w_i$ is the number of electrons in fragment i with the mean excitation energy $I_{0i}$ and

$$\sum_i w_i = n \tag{10}$$

is the total number of electrons in the system.

If one considers a diatomic molecule $X_2$ to consist of two fragments $X^+$ and $X^-$ with N+1 and N-1 electrons, respectively, we may apply Eq. (9) to calculate the mean excitation energy of the diatomic molecule $X_2$ from the mean excitation energies of the two ions $X^+$ and $X^-$. However, Eq. (9) also implies that Bragg's rule predicts that the mean excitation energy of the homonuclear, diatomic molecule $X_2$ is the same as that of the atom X. Thus, applying Eq. (10) twice for an atom with charge q one may calculate the mean excitation energy of the atom from the $I_0$'s of ions with charges q-1 and q+1 as

$$2NlnI_0^q = (N+1)lnI_0^{q+1} + (N-1)lnI_0^{q-1} \tag{11}$$

Equation (11) with q = 0 has been used to calculate the mean excitation energies for the neutral atom listed in column 9 of Table 2. The difference between the calculated values of $I_0$ and those obtained by applying Bragg's rule is also listed in Table 2. We can see that Bragg's rule tend to underestimate the directly calculated mean excitation energies of the neutral atoms by 4-6 eV. However, for many experimental purposed this may be acceptable accuracy.

Thus, Eq. (11) may provide another method for obtaining one of the three mean excitation energies from the two "neighboring" ions/atoms. An application of Eq. (11) could be to calculate the mean excitation energy of the negative ions of He, Be, Ne, Mg, and Ar, that is the ions for which we could not calculate them with the RPA method. Inserting the $I_0$'s of the neutral and singly charged positive ions of these atoms[8] in Eq. (11) we find that $I_0(He^-)$ = 38 eV, $I_0(Be^-)$ = 29 eV, $I_0(Ne^-)$ = 118 eV, $I_0(Mg^-)$ = 99 eV, and $I_0(Ar^-)$ = 165 eV. Another way to estimate the same mean excitation energies would be an application of the "3/4 rule-of-thumb" mentioned above to calculate the mean excitation energies of the anions from $I_0$ of the neutral atoms[8]. The results of such a calculation are $I_0(He^-)$ = 32 eV, $I_0(Be^-)$ = 32 eV , $I_0(Ne^-)$ = 103 eV, $I_0(Mg^-)$ = 96 eV , and $I_0(Ar^-)$ = 142 eV. The two set of results are thus of the same order of magnitude for 5 unstable anions and may serve as a first guess on the mean excitations energies that we were unable to calculate.

## *6. Summary*

Using the Random- Phase approximation we have calculated all excitation energies and oscillator strengths in large basis sets for singly charged anions of nitrogen and the atoms with Z ≤ 18 that have positive electron affinity. From the sum-over-states expressions in Eq. (2) we have then computed the mean excitations of the negative ion.

It turns out that with a few exceptions the variation with Z is similar for singly charged anions, neutral atoms and single charged positive ions, see Fig.1. This allows us to estimate the – often unknown - mean excitation energies of negative ions from the more available mean excitation energies of neutral atoms[24]. In most cases one may obtain the mean excitation energy of an ion by multiplying $I_0$ of the atom/ion with the same nuclear charge but one electron less by a factor of 3/4.

We have also shown that Bragg's rule[30] applied to ions may be applied to predict mean excitation energies with charge q from those with charges q±1, see Eq. (11). This method was used to estimate values for mean excitation energies of the unstable singly charged anions for which we could not obtain convergence of the RPA calculation.

Thus, the main conclusion of our calculations is that there exist rather simple rules that relate the mean excitation energies of atoms with different charges but the same value of nuclear charge Z.

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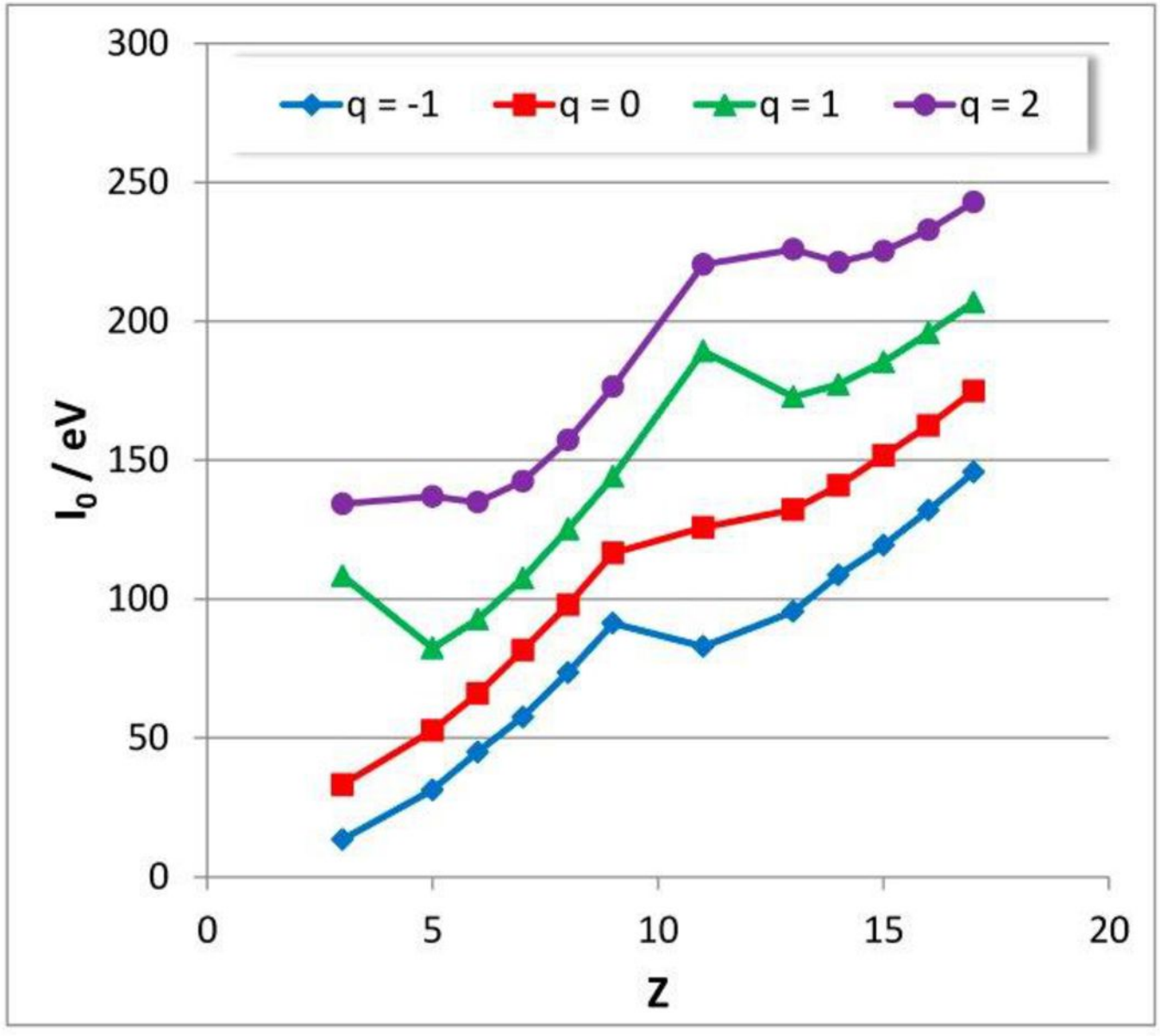
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200
150
100
50
0
$I_0$ / eV
0
5
10
15
20
Z
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q = 1
q = 2