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Z-dependence of Mean Excitation Energies for Second and Third Row Atoms and Their Ions

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Abstract

All mean excitation energies for second and third row atoms and their ions are calculated in the random-phase approximation using large basis sets. To a very good approximation it turns out that mean excitation energies within an isoelectronic series is a quadratic function of the nuclear charge. It is demonstrated that this behavior is linked to the fact that the contributions from continuum electronic states give the dominate contributions to the mean excitation energies and that these contributions for atomic ions appear hydrogen-like. We argue that this finding may present a method to get a first estimate of mean excitation energies also for other non-relativistic atomic ions.

1. Introduction

The slowing down of a swift projectile with energy in the MeV range when impinging on a target of atoms, molecules or solids is caused primarily by electronic excitation of the electrons in the target by transfer of projectile kinetic energy to target electronic energy. This has been known since Bethe first derived the basic theory for this process¹. Also, one of the most interesting findings is that the only essential material constant determining the slowing down or stopping power of the target is a weighted average of all the target electronic excitation energies, referred to as the mean excitation energy. Thus, the stopping of heavy charged particles in matter is basically an electronic structure problem and application of known methods of electronic structure theory that are able to calculate *all* electronic excitation energies of a given atom or molecule may straightforwardly be applied to this problem²⁻⁵.

The range of electronic excitation energies needed to calculate the mean excitation energy as well as many other sum over states molecular properties^{6,7} includes both bound and continuum states and for many properties, for all atoms and molecules, the major contribution to the mean excitation energy originates from electron excitations into the continuum. Luckily, it turns out that a stick-spectrum representation of the continuum in terms of pseudo-states placed in the continuum suffices when calculating atomic and molecular mean excitation energies⁸, which means that one may apply standard finite basis set methods also when calculating the continuum contributions to the mean excitation energies. However, rather large and flexible basis sets as well as inclusion of all excited states in the sum over states expressions are needed in order to obtain converged results for the computed mean excitation energies.

The loss of kinetic energy of a proton projectile per unit path length is referred to as the stopping power of the target material and this quantity is of central importance for the understanding of many fundamental

processes. For years, X-ray beams have been used for medical purposes such as for cancer therapy, but more recently therapy has carried out using heavy, massive particle beams such as proton beams which allows for considerable reduction of the collateral damage of surrounding tissue associated with radiative treatment^{9,10} due to the narrowness of the peak in the stopping power curve as a function of projectile energy for particle beams.

However, the focus of this paper is the application of mean excitation energies – and thus stopping power data – to materials where the target itself consists of a mixture of charged particles, i.e. plasmas. Targets of this sort may be found in fields such as reactor physics¹¹, planetary atmospheres¹², and interstellar space¹³. In these fields one often needs to know the stopping power for many ionized states of an atom. Thus, it is the purpose of this paper to calculate these mean excitation energies for all atoms for which we can safely neglect relativistic effects in the electronic structure calculations and also to derive simple rules that allow one to derive the mean excitation energy of any ionized form of an atom from the knowledge of the mean excitation energy of the neutral atom or any other ion in an isoelectronic series.

We first give an outline of the definition and the application of mean excitation energy followed by a description of the method used to calculate them. We report mean excitation energies for all second and third row atoms and their ions, and the rest of the paper deals with the systematics and the explanation of the nuclear charge (Z) dependence of the atomic ion mean excitation energies.

2. Definitions

The central material constant in the theory of stopping power, the mean excitation energy, is defined as

$$I_0 = \exp\left(\frac{\sum_{n \neq 0} f_{n0} \ln(E_{n0})}{\sum_{n \neq 0} f_{n0}}\right) \quad (1)$$

Here, $E_{n0} = E_n - E_0$ is the excitation energy between the ground state $|0\rangle$ and the excited state $|n\rangle$ and f_{n0} is the electric dipole oscillator strength for the same excitation which in the dipole length approximation using atomic units is defined as

$$f_{n0} = \frac{2}{3} \langle 0 | \mathbf{r} | n \rangle \cdot \langle n | \mathbf{r} | 0 \rangle E_{n0} \quad (2)$$

The summations in Eq. (1) extend over all excited states, bound as well as continuum. For the continuum states, the summation should have been integration but for simplicity we have used the summation sign for all states as is the practice in finite basis set calculations where the integration over the continuum states is replaced by a summation over discrete pseudo states placed in the continuum (*vide infra*).

3. Details of the Calculations

All calculations have been carried out with the Dalton program package¹⁴ at the level of the random-phase approximation (RPA). In practice, the calculations on the open shell atoms or ions were carried out as MCSCF calculations with one configuration corresponding to one of the states of the atomic term. For every atom or ion all excitation energies and the corresponding dipole oscillator strengths were calculated

in the given basis set and the mean excitation energy was then computed as a sum over states according to Eq. (1). A majority of the excited states were placed in the continuum.

Based on our previous basis set studies^{3,5,15,16} we adopted the largest correlation-consistent basis sets of Dunning and co-workers¹⁷ as one-electron basis sets. For B to F the Dunning's core-valence correlation consistent basis set aug-cc-pCV5Z was employed, for Al to Ar the fully uncontracted aug-cc-pCV5Z. For Li and Be the fully uncontracted aug-cc-pCVQZ and for Na and Mg the fully uncontracted cc-pCV5Z basis sets had to be used, as an aug-cc-pCV5Z has not yet been published. The Thomas-Reiche-Kuhn sum rule¹⁸,

$$\sum_{n \neq 0} f_{n0} = N \quad (3)$$

in which N is the number of electrons, was fulfilled for all the studied atoms and their ions to at least two decimal places in the length, mixed and velocity representations. Also the mean excitation energies are the same to three digits in the three representations. Although this equivalence is not a sufficient condition it is nevertheless a necessary condition for basis set completeness in RPA¹⁹.

4. Results

The calculated mean excitation energies in the dipole length formulation in RPA are reported in Tables 1-18 for all second and third row atoms and their ions. For completeness sake we have also added RPA results from previous calculations^{8,20} for first row atoms and ions in Table 1 and 2. In order to illustrate better the systematics of the Z-dependence of the mean excitation energies each table contains mean excitation energy for one isoelectronic series only. In fact, the table numbering is the same as the number of electrons in the isoelectronic series which we will refer to as N in the rest of the text.

In order to determine more precisely how the calculated mean excitation energies in an isoelectronic series depends on Z we first notice that the mean excitation energy for a hydrogen-like, one-electron atomic ion is^{21,22}

$$I_0 = Z^2 I_0(\text{H}) \quad (4)$$

Let us next consider how well this relationship – in a modified form – holds for the rest of the ions. To this end we express the computed mean excitation energy as

$$I_0 = Z_{\text{eff}}^2 I_0(\text{H}) \quad (5)$$

with Z_{eff} being

$$Z_{\text{eff}} = Z - S \quad (6)$$

One may view S as a screening constant, but as we shall see later, this interpretation does not hold for all ions.

The quantities Z_{eff} and S as well as the differences in S from one ion to the next, when different from zero, are also given in Tables 1-18.

Table 1. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 1-electron ions with electron configuration $1s^1$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$
H	14.99 ^{c)}	1.00	0.00
He ⁺	59.88 ^{d)}	2.00	0.00
Li ²⁺	134.5	2.99	0.01
Be ³⁺	240.2	4.00	0.00
B ⁴⁺	374.6	5.00	0.00
C ⁵⁺	539.5	6.00	0.00
N ⁶⁺	734.3	7.00	0.00
O ⁷⁺	959.0	8.00	0.00
F ⁸⁺	1213.7	9.00	0.00
Ne ⁹⁺	1498.4	10.00	0.00
Na ¹⁰⁺	1813.9	11.00	0.00
Mg ¹¹⁺	2158.8	12.00	0.00
Al ¹²⁺	2533.5	13.00	0.00
Si ¹³⁺	2938.3	14.00	0.00
P ¹⁴⁺	3373.1	15.00	0.00
S ¹⁵⁺	3837.8	16.00	0.00
Cl ¹⁶⁺	4332.5	17.00	0.00
Ar ¹⁷⁺	4857.2	18.00	0.00

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) RPA value from reference 8

d) RPA value from reference 20

Table 2. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 2-electron ions with electron configuration $1s^2$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$
He	42.68 ^{c)}	1.69	0.31
Li ¹⁺	108.3	2.69	0.31
Be ²⁺	205.0	3.70	0.30
B ³⁺	330.4	4.69	0.31
C ⁴⁺	486.2	5.70	0.30
N ⁵⁺	672.0	6.70	0.30
O ⁶⁺	887.8	7.70	0.30
F ⁷⁺	1133.5	8.70	0.30
Ne ⁸⁺	1409.2	9.70	0.30
Na ⁹⁺	1715.6	10.70	0.30

Mg ¹⁰⁺	2051.5	11.70	0.30
Al ¹¹⁺	2417.2	12.70	0.30
Si ¹²⁺	2813.0	13.70	0.30
P ¹³⁺	3238.8	14.70	0.30
S ¹⁴⁺	3694.5	15.70	0.30
Cl ¹⁵⁺	4180.2	16.70	0.30
Ar ¹⁶⁺	4695.9	17.70	0.30

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) RPA value from reference 20

Table 3. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 3-electron atom and ions with electron configuration $1s^2 2s^1$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	S ^{b)}	$\Delta S^{\text{c)}}$
Li	33.1	1.49	1.51	
Be ¹⁺	76.9	2.26	1.74	0.22
B ²⁺	136.9	3.02	1.98	0.24
C ³⁺	214.2	3.78	2.22	0.24
N ⁴⁺	308.7	4.54	2.46	0.24
O ⁵⁺	420.7	5.30	2.70	0.24
F ⁶⁺	550.0	6.06	2.94	0.24
Ne ⁷⁺	696.8	6.82	3.18	0.24
Na ⁸⁺	861.2	7.58	3.42	0.24
Mg ⁹⁺	1043.2	8.34	3.66	0.24
Al ¹⁰⁺	1242.7	9.10	3.90	0.24
Si ¹¹⁺	1459.8	9.87	4.13	0.24
P ¹²⁺	1694.6	10.63	4.37	0.24
S ¹³⁺	1947.0	11.40	4.60	0.24
Cl ¹²⁺	2217.2	12.16	4.84	0.24
Ar ¹⁵⁺	2505.0	12.93	5.07	0.23

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 4. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 4-electron atom and ions with electron configuration $1s^2 2s^2$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	S ^{b)}	$\Delta S^{\text{c)}}$
Be	42.2	1.68	2.32	
B ¹⁺	82.3	2.34	2.66	0.34
C ²⁺	134.8	3.00	3.00	0.34

N ³⁺	200.2	3.65	3.35	0.34
O ⁴⁺	278.6	4.31	3.69	0.34
F ⁵⁺	370.2	4.97	4.03	0.34
Ne ⁶⁺	475.0	5.63	4.37	0.34
Na ⁷⁺	593.3	6.29	4.71	0.34
Mg ⁸⁺	724.8	6.95	5.05	0.34
Al ⁹⁺	869.6	7.62	5.38	0.34
Si ¹⁰⁺	1027.9	8.28	5.72	0.34
P ¹¹⁺	1199.7	8.95	6.05	0.33
S ¹²⁺	1384.9	9.61	6.39	0.33
Cl ¹³⁺	1583.7	10.28	6.72	0.33
Ar ¹⁴⁺	1796.0	10.95	7.05	0.33

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 5. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 5-electron atom and ions with electron configuration $1s^2 2s^2 2p^1$.

Ion	I_0 [eV]	Z_{eff} ^{a)}	S ^{b)}	ΔS ^{c)}
B	52.6	1.87	3.13	
C ¹⁺	92.6	2.49	3.51	0.39
N ²⁺	142.4	3.08	3.92	0.40
O ³⁺	202.2	3.67	4.33	0.41
F ⁴⁺	272.3	4.26	4.74	0.41
Ne ⁵⁺	352.6	4.85	5.15	0.41
Na ⁶⁺	443.5	5.44	5.56	0.41
Mg ⁷⁺	544.8	6.03	5.97	0.41
Al ⁸⁺	656.4	6.62	6.38	0.41
Si ⁹⁺	778.6	7.21	6.79	0.41
P ¹⁰⁺	911.2	7.80	7.20	0.41
S ¹¹⁺	1054.5	8.39	7.61	0.41
Cl ¹²⁺	1208.2	8.98	8.02	0.41
Ar ¹³⁺	1372.6	9.57	8.43	0.41

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 6. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 6-electron atom and ions with electron configuration $1s^2 2s^2 2p^2$.

Ion	I_0 [eV]	Z_{eff} ^{a)}	S ^{b)}	ΔS ^{c)}
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C	65.9	2.10	3.90	
N ¹⁺	107.4	2.68	4.32	0.42
O ²⁺	157.2	3.24	4.76	0.44
F ³⁺	215.6	3.79	5.21	0.45
Ne ⁴⁺	282.8	4.34	5.66	0.45
Na ⁵⁺	358.7	4.89	6.11	0.45
Mg ⁶⁺	443.8	5.44	6.56	0.45
Al ⁷⁺	537.4	5.99	7.01	0.45
Si ⁸⁺	640.1	6.53	7.47	0.45
P ⁹⁺	751.7	7.08	7.92	0.45
S ¹⁰⁺	872.2	7.63	8.37	0.45
Cl ¹¹⁺	1001.8	8.17	8.83	0.45
Ar ¹²⁺	1140.3	8.72	9.28	0.45

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 7. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 7-electron atom and ions with electron configuration $1s^2 2s^2 2p^3$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$	$\Delta S^{\text{c)}}$
N	81.6	2.33	4.67	
O ¹⁺	125.2	2.89	5.11	0.44
F ²⁺	176.4	3.43	5.57	0.46
Ne ³⁺	235.2	3.96	6.04	0.47
Na ⁴⁺	301.9	4.49	6.51	0.47
Mg ⁵⁺	376.7	5.01	6.99	0.47
Al ⁶⁺	459.2	5.53	7.47	0.48
Si ⁷⁺	549.7	6.06	7.94	0.48
P ⁸⁺	648.2	6.58	8.42	0.48
S ⁹⁺	754.6	7.10	8.90	0.48
Cl ¹⁰⁺	869.1	7.61	9.39	0.48
Ar ¹¹⁺	991.6	8.13	9.87	0.48

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 8. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 8-electron atom and ions with electron configuration $1s^2 2s^2 2p^4$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$	$\Delta S^{\text{c)}}$
O	97.9	2.56	5.44	
F ¹⁺	144.0	3.10	5.90	0.46

Ne ²⁺	196.9	3.62	6.38	0.47
Na ³⁺	256.8	4.14	6.86	0.49
Mg ⁴⁺	324.3	4.65	7.35	0.49
Al ⁵⁺	398.8	5.16	7.84	0.49
Si ⁶⁺	480.6	5.66	8.34	0.50
P ⁷⁺	569.7	6.16	8.84	0.50
S ⁸⁺	666.2	6.67	9.33	0.50
Cl ⁹⁺	769.9	7.17	9.83	0.50
Ar ¹⁰⁺	881.1	7.67	10.33	0.50

^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

^{c)} ΔS is the difference in S between the entry in preceding row and in this row.

Table 9. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 9-electron atom and ions with electron configuration $1s^2 2s^2 2p^5$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}$	S ^{b)}	$\Delta S^{\text{c)}$
F	116.5	2.79	6.21	
Ne ¹⁺	165.2	3.32	6.68	0.47
Na ²⁺	220.4	3.83	7.17	0.49
Mg ³⁺	282.5	4.34	7.66	0.49
Al ⁴⁺	351.0	4.84	8.16	0.50
Si ⁵⁺	426.5	5.33	8.67	0.50
P ⁶⁺	508.8	5.83	9.17	0.51
S ⁷⁺	598.0	6.32	9.68	0.51
Cl ⁸⁺	694.0	6.80	10.20	0.51
Ar ⁹⁺	797.0	7.29	10.71	0.51

^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

^{c)} ΔS is the difference in S between the entry in preceding row and in this row.

Table 10. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 10-electron atom and ions with electron configuration $1s^2 2s^2 2p^6$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}$	S ^{b)}	$\Delta S^{\text{c)}$
Ne	137.2	3.03	6.97	
Na ¹⁺	189.2	3.55	7.45	0.47
Mg ²⁺	246.8	4.06	7.94	0.49
Al ³⁺	310.8	4.55	8.45	0.50
Si ⁴⁺	381.4	5.04	8.96	0.51
P ⁵⁺	458.5	5.53	9.47	0.51
S ⁶⁺	542.1	6.01	9.99	0.52
Cl ⁷⁺	632.1	6.49	10.51	0.52

Ar ⁸⁺	728.8	6.97	11.03	0.52
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^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

^{c)} ΔS is the difference in S between the entry in preceding row and in this row.

Table 11. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 11-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^1$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}$	$S^{\text{b)}$	$\Delta S^{\text{c)}$
Na	125.7	2.90	8.10	
Mg ¹⁺	173.7	3.40	8.60	0.49
Al ²⁺	225.8	3.88	9.12	0.52
Si ³⁺	283.1	4.35	9.65	0.54
P ⁴⁺	345.9	4.80	10.20	0.54
S ⁵⁺	414.4	5.26	10.74	0.55
Cl ⁶⁺	488.6	5.71	11.29	0.55
Ar ⁷⁺	568.6	6.16	11.84	0.55

^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

^{c)} ΔS is the difference in S between the entry in preceding row and in this row.

Table 12. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 12-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^2$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}$	$S^{\text{b)}$	$\Delta S^{\text{c)}$
Mg	128.0	2.92	9.08	
Al ¹⁺	172.7	3.39	9.61	0.53
Si ²⁺	221.2	3.84	10.16	0.55
P ³⁺	274.3	4.28	10.72	0.56
S ⁴⁺	332.4	4.71	11.29	0.57
Cl ⁵⁺	395.5	5.14	11.86	0.57
Ar ⁶⁺	463.9	5.56	12.44	0.57

^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

^{c)} ΔS is the difference in S between the entry in preceding row and in this row.

Table 13. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 13-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^1$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$	$\Delta S^{\text{c)}}$
Al	132.2	2.97	10.03	
Si ¹⁺	177.2	3.44	10.56	0.53
P ²⁺	225.2	3.88	11.12	0.56
S ³⁺	277.3	4.30	11.70	0.58
Cl ⁴⁺	333.8	4.72	12.28	0.58
Ar ⁵⁺	394.9	5.13	12.87	0.59

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 14. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 14-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^2$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$	$\Delta S^{\text{c)}}$
Si	140.8	3.06	10.94	
P ¹⁺	185.3	3.52	11.48	0.55
S ²⁺	232.8	3.94	12.06	0.57
Cl ³⁺	284.1	4.35	12.65	0.59
Ar ⁴⁺	339.4	4.76	13.24	0.59

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 15. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 15-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^3$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$	$\Delta S^{\text{c)}}$
P	151.6	3.18	11.82	
S ¹⁺	195.7	3.61	12.39	0.57
Cl ²⁺	242.9	4.03	12.97	0.59
Ar ³⁺	293.7	4.43	13.57	0.60

a) The effective charge defined in Eq. (5).

b) The S parameter is defined in Eq. (6).

c) ΔS is the difference in S between the entry in preceding row and in this row.

Table 16. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 16-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^4$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	$S^{\text{b)}}$	$\Delta S^{\text{c)}}$
S	162.4	3.29	12.71	

Cl ¹⁺	206.8	3.71	13.29	0.58
Ar ²⁺	254.0	4.12	13.88	0.60

^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

^{c)} ΔS is the difference in S between the entry in preceding row and in this row.

Table 17. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 17-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^5$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	S ^{b)}	$\Delta S^{\text{c)}$
Cl	174.9	3.42	13.58	
Ar ¹⁺	219.5	3.83	14.17	0.59

^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

^{c)} ΔS is the difference in S between the entry in preceding row and in this row.

Table 18. Mean excitation energy, I_0 (in eV), effective charge and shielding constant S of the 18-electron atom and ions with electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$.

Ion	I_0 [eV]	$Z_{\text{eff}}^{\text{a)}}$	S ^{b)}
Ar	188.7	3.55	14.45

^{a)} The effective charge defined in Eq. (5).

^{b)} The S parameter is defined in Eq. (6).

In the random-phase approximation electron correlation is included through first order in the fluctuation potential for both the ground and excited states²³. It has been our experience that this level of theory is sufficient to obtain reliable mean excitation energies. That this in fact also is the case for the atoms and ions we are concerned with here can also be seen from comparison with the more correlated, Second-Order Polarization Propagator(SOPPA)²³ calculations on Be that gave $I_0 = 43.6 \text{ eV}^{24}$. Also SOPPA calculations for some aluminum ions²⁵ resulted in mean excitation energies that are within a couple of eV's of those reported here, the small difference most likely being due to the use of smaller one-electron basis sets being applied in the SOPPA calculations²⁵. Finally, correlated coupled cluster based calculations on the noble gases¹⁶ in basis set of the same quality as the ones used here showed that the including correlation at the CCSD level only reduced the RPA values with 1.8 eV for Ne and 2.2 eV for Ar.

Since electron correlation is included in an RPA calculation it is not possible to break the computed mean excitation energies up into orbital contributions as it would have been in for example a Hartree-Fock calculation, the accuracy of which on the other hand would not have been sufficient for our purpose. This also has the consequence that orbital differences in the screening abilities of the individual electrons are averaged out in the Z_{eff} parameter and it thus becomes less appropriate to refer to it as screening constant as we shall discuss later.

5. Z-dependence of the mean excitation energies

In Figure 1 we have plotted the Z-dependence of the mean excitation energies of the neutral atoms. For completeness we have also included the exact mean excitation energy of the hydrogen atom, $I_0(\text{H}) = 14.990 \text{ eV}$ ²¹ as well as the RPA-value for He²⁰.

The basic trend in Fig. 1 is a monotonic increase in I_0 with increasing nuclear charge of the atom, the exception being the noble gases which have larger mean excitation energy than the subsequent alkali metal. Another way of expressing the trend in Fig. 1 would be to say that the mean excitation energies in a row form a monotonically increasing series. As the stopping power is inversely proportional to the logarithm of the mean excitation energy^{4,22} we can conclude that the ability of a neutral atom to slow down an incoming fast projectile at a given velocity decreases as the atomic charge is increasing and that this effect is a monotonic function of Z, the noble gases being the exception to this general trend.

Figure 1 also displays the shell structure of the neutral atoms as the curve is rather similar in structure for the second and third row atoms. One may notice though that the increase in I_0 with Z levels of going from first to second and third row atoms.

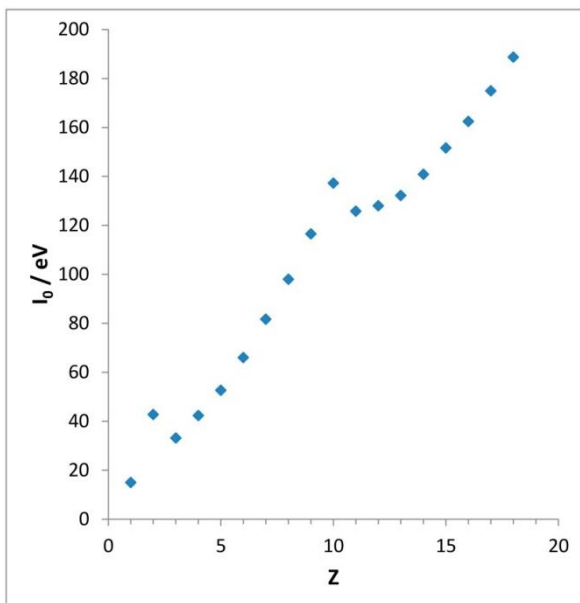


Figure 1. The mean excitation energy I_0 (in eV) for neutral atoms as a function of the nuclear charge Z.

For all the atomic ions, we see from Tables 1-18 that the mean excitation energy of the ions in any isoelectronic series increases with nuclear charge. This is an effect of the electrons being pulled closer to the nucleus as its charge increases and is illustrated for the C-isoelectronic in Fig. 2. This behavior of I_0 in turn also implies that the stopping power of atomic ions will decrease along an isoelectronic series.

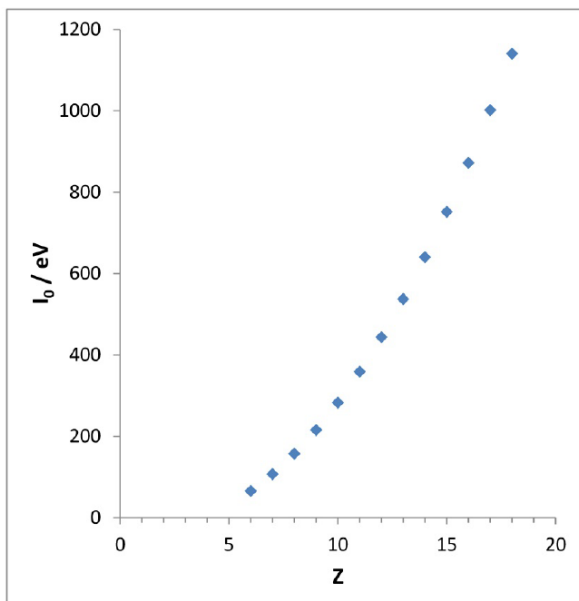


Figure 2. The mean excitation energy I_0 (in eV) for the 6-electron isoelectronic series (data from Table 6).

Comparing Fig. 1 with Tables 1-18 and Fig. 2 we see that the changes in I_0 with Z are considerably more pronounced for atomic ions than for neutral atoms.

From Table 1 we see, as expected, that $S = 0.00$ in Eq. (5) for one-electron ions, indicating that the computed mean excitation energies are in agreement with Eq.(4) and thus correct for this series. For all the two-electron ions in both rows (Table 2), the screening constant is 0.30, *i.e.* equal to Slater's originally suggested value for the 1s-shell²⁶, a somewhat surprising result in view of the fact that this screening constant was suggested for a very different purpose than the present. Thus, irrespective of the charge of the central atom the same screening constant may be applied when calculating K-shell mean excitation energies.

For the rest of the isoelectronic series we see that the screening constant is increasing with increasing nuclear charge of the atom. However, rather early on in the isoelectronic series, S becomes larger than the number of electrons in the series (for instance for Ne^{7+} in the 3-electron series) so it loses its meaning as a "screening constant" and becomes merely a parameter describing the computed mean excitation energies in terms of Eqs. (5) and (6).

From Tables 2-18 we also see that the increase in S is (nearly) constant going from one ion to the next in a given isoelectronic series. Only for the lowest charged ion(s) in the isoelectronic series do we see a minor deviation from this constancy. Also, the constant is the same for both second and third row ions.

The increases in S with increasing nuclear charge differ from one isoelectronic series to another, starting with 0.24 for 3-electron ions and ending up with close to 0.60 for the isoelectronic series with most electrons for which we can reliably extract values for from the present data set of mean excitation energies.

Thus, we have the following linear relationship between the S parameter of the ion $S_N(Z)$ and that of the neutral atom $S_N(N = Z) \equiv S_{N0}$

$$S_N(Z) = S_{N0} + (Z - N)D_N \quad (7)$$

where $N = 1,2,3,4 \dots$ labels the number of electrons in the isoelectronic series and thus N must be smaller than or equal to Z in order for Eq.(7) to be valid. Please note that Eq. (7) also holds for the 1-electron ions for which both S_{N0} and D_N are zero and for the 2-electron isoelectronic series where the values of S_{N0} and D_N are 0.30 and 0.00, respectively. The D_N constants in Eq. (7) can be extracted from Tables 1-18 and are given in Table 19.

Inserting Eqs. (6) and (7) into Eq. (5) we find that the mean excitation energy for an ion with nuclear charge Z in the N-electron isoelectronic series, $I_{0N}(Z)$, may be calculated from the equation

$$\frac{I_{0N}(Z)}{I_{0(H)}} = A_N Z^2 + B_N Z + C_N \quad (8)$$

where

$$A_N = (1 - D_N)^2 \quad (9)$$

$$B_N = 2(1 - D_N)(ND_N - S_{N0}) \quad (10)$$

and

$$C_N = (ND_N - S_{N0})^2 \quad (11)$$

Thus, for a given isoelectronic series, the mean excitation energy of any ion in the series is a quadratic function of the nuclear charge and the mean excitation energy can be computed from one constant D_N and the mean excitation energy of the *neutral* ($N=Z$) atom, I_{0N} , since the constant S_{N0} in Eqs. (9) and (10) is related to I_{0N} as

$$S_{N0} = N - \sqrt{\frac{I_{0N}}{I_{0(H)}}} \quad (12)$$

The constants in Eq. (8) are given in Table 19. The Table lists only the parameters for the isoelectronic series for which our calculations give converged values of the S parameter in Eq. (6).

Table 19. The parameters needed for an approximate calculation of the mean excitation energy of atomic ions in an isoelectronic series with N electrons, according to Equation (8).

N	D_N	S_{N0}	A_N	B_N	C_N
1	0	0	1	0	0
2	0.00	0.30	1.00	-0.60	0.09
3	0.24	1.51	0.58	-1.20	0.62
4	0.34	2.32	0.44	-1.27	0.92
5	0.41	3.13	0.35	-1.27	1.17
6	0.45	3.90	0.30	-1.32	1.44

7	0.48	4.67	0.27	-1.36	1.72
8	0.50	5.44	0.25	-1.44	2.07
9	0.51	6.21	0.24	-1.60	2.66
10	0.52	6.97	0.23	-1.69	3.13
11	0.55	8.10	0.20	-1.85	4.20
12	0.57	9.08	0.18	-1.93	5.02
13	0.58	10.03	0.18	-2.09	6.20
14	0.59	10.94	0.17	-2.68	10.69

Since the ΔS are not exactly constant for an isoelectronic series, application of Eq. (8) will not give precisely the mean excitation energies in Tables 1-18. For example, the mean excitation energy calculated from Eq. (8) for Al^{5+} is 384 eV compared with 399 eV from Table 8. The predictive potential of Eq. (8) can be improved if one of the more ionized ions in the isoelectronic series is used as the preliminary ion from which the rest of the mean excitation energies in the isoelectronic series are calculated from according to a slightly modified version of Eq. (8). For instance, calculating $I_0(Al^{5+})$ from $I_0(Na^{3+})$ rather than from $I_0(O)$ as above using a modified version of Eq. (8) yields $I_0(Al^{5+}) = 396$ eV in considerable better agreement with the value in Table 8. The modified version of Eq. (8) used in the latter calculation is obtained from Eq. (8) by replacing N by $N + k$ and S_{N0} by S_{Nk} in both Eqs. (10) and (11). Here, k is the number of ΔS steps that the new reference ion with mean excitation energy I_{0k} lies away from the neutral atom in the isoelectronic series. In the preceding example $k = 3$.

Thus, application of Eq. (8) can give improved values for the mean excitation energy if one uses a reference mean excitation energy for an ion in the isoelectronic series for which ΔS has converged. This of course requires that I_0 is known for the reference ion.

6. Discussion

We have designed a method to calculate mean excitation energies for highly ionized atoms in an isoelectronic series from I_0 of neutral atom or - perhaps even better - slightly ionized atoms. The method relies upon the observation that the atomic mean excitation energy in an isoelectronic series to a very good approximation turns out to be a quadratic function of the nuclear charge Z , see Eq. (8) and Table 19.

In order to better understand this behavior we first notice that for a hydrogen-like, 1-electron atom the oscillator strength in Eq. (2) is independent of nuclear charge since the Z -dependence of the individual transition moments are Z^{-1} while the excitation energies are proportional to Z^2 . However, also the calculated oscillator strengths for an isoelectronic series turned out to be nearly independent of Z , in particular for all higher lying excited states, i.e. for excitations into the pseudo continuum states that gives the dominate contributions to the mean excitation energy⁸. The Z -independence of f_{n0} works best for ions with some charge, that is, ions for which D_N becomes constant. For an electron in a high-lying continuum state the atomic core will look very much hydrogen-like and that is probably the reason why we see the same Z -independence of the oscillator strengths for those states as one finds for a hydrogen-like system.

Thus, from the definition in Eq. (1) it follows that the Z-dependence of the mean excitation energies in an atomic isoelectronic series is primarily determined by the Z-dependence of the excitation energies – and among those, the excitation energies of the higher lying continuum states. As argued previously an electron in these states will experience a hydrogen-like core and thus its excitation energy is determined through the approximate relation that resembles that in Eq. (4)

$$E_{n0}(N,Z) \sim (Z-S_N(Z))^2 E_{n0}(Z=N) \quad (13)$$

where $S_N(Z)$ is given in Eq. (7). Following this line of argumentation the increase in $S_N(Z)$ for the N-electron isoelectronic series with increasing Z may be explained as an increasing ability of the N electrons to screen the atomic core as Z is increasing. Furthermore, this screening ability will increase with N, thus resulting in the increase in D_N we are seeing in Table 19.

We have tested the validity of Eq. (13) by calculating the individual excitation energies that contribute to the mean excitation energies in an isoelectronic series to see if they in fact obey Eq. (13). More specifically, we have calculated the ratio $E_{n0}(N,Z)/E_{n0}(N, Z+1)$ for a given N and all states $|n\rangle$ as a function of Z. If the assumption in Eq. (13) holds this ratio must be equal the ratios between the square of $Z_{\text{eff}}/(Z+1)_{\text{eff}}$ taken from Table N which in fact turns out to be the case to a very good approximation. The larger Z becomes the better the relation is fulfilled.

The relationship between I_{0N} and Z for an N-electron isoelectronic series in Eq. (8) is based on computed, accurate mean excitation energies for second and third row atoms and their ions. However, since the origin of this relationship seems to be that an electron in a high-lying continuum state sees the core as a screened, hydrogen-like core it likely that Eq. (8) also will hold for isoelectronic series of atoms in higher rows of the periodic table as long as one may safely disregard relativistic effects. So, knowing one mean excitation energy in an isoelectronic series a first estimate of the rest of the mean excitation energies in the same isoelectronic series may be obtained from Eq. (8) and the constants in Table 19 for isoelectronic series with electrons smaller than 15, i.e. for K and L shell ions. This may provide useful information in plasma and reactor physics where it often is necessary to know stopping powers for a range of atomic ions^{11,27}. As explained in Sec. 5 one need not know the mean excitation of the neutral atom in order to make use of Eq. (8). Knowledge of I_0 of any ion in the series will do.

As the origin of the quadratic behavior of I_0 as a function of Z in a given isoelectronic series may be traced back to the two observations that the bulk of the contributions to I_0 originates from high-lying continuum states and that these states are hydrogen-like then similar relationship between sum rules and Z in isoelectronic series most likely also will hold for other dipole oscillator strength sum rules that are determined by primarily continuum contributions⁸, i.e. S_n and L_n sum rules for $n \geq 0$.

7. Conclusions

We have reported accurate calculations of mean excitation energies for all second and third row atoms and atomic ions using the random-phase approximation and large one-electron basis sets. An analysis of the computed results revealed that mean excitation energies within an isoelectronic series to a very good approximation were quadratic functions of the nuclear charge Z. The more precise relationship is given in

Eq. (8) and Table 9. We also argue that the background for this relationship is that for electrons in high-lying continuum states the ion core appears hydrogen-like. This in turns implies that the validity of the quadratic relationship in Eq. (8) may be extended beyond the second and third row of the periodic system.

References

- 1 H. Bethe, *Ann. Phys.* 397, 325 (1930).
- 2 R. C. Trujillo, J. R. Sabin, and J. Oddershede, *Adv. Quantum Chem.* 46, 121 (2004).
- 3 S. P. A. Sauer, J. Oddershede, and J. R. Sabin, *J. Phys. Chem. A* 110, 8811 (2006).
- 4 J. R. Sabin, J. Oddershede, and S. P. A. Sauer, *Adv. Quantum Chem.* 65, 63 (2013).
- 5 P. W. K. Jensen, S. P. A. Sauer, J. Oddershede, and J. R. Sabin, *Nucl. Instr. Meth. Phys. Res. B* 394, 73 (2017).
- 6 W. J. Meath and A. Kumar, *Intern. J. Quantum Chem.* S24, 501 (1990).
- 7 A. Kumar and W. J. Meath, *Mol. Phys.* 77, 311 (1992).
- 8 J. Oddershede, J. F. Ogilvie, S. P. A. Sauer, and J. R. Sabin, *Adv. Quantum Chem.* 75, 229 (2017).
- 9 C. von Sonntag, *The Chemical Basis for Radiation Biology*, Taylor and Francis, London (1987).
- 10 P. Andreo, *Phys. Med. Biol.* 54, N209 (2009).
- 11 N. Rostocker, M. Binderbauer, and H. J. Monkhorst, *Science* 278, 1419 (2014).
- 12 J. L. Fox, M. I. Garland, and R. E. Johnson, *Space Sci. Rev.* 139, 3 (2008).
- 13 O. Martinez Jr., T. P. Snow, and V. M. Bierbaum, *Ion Chemistry in the Interstellar Medium*, Proc. IAU Symposium No. 251, 139 (S. Kwok and S. Sandford, Eds.) (2008).
- 14 K. Aidas, C. Angeli, K. L. Bak, V. Bakken, L. Boman, O. Christiansen, R. Cimraglia, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekstrøm, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernandez, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hetttema, S. Høst, I-M. Høyvik, M. F. Iozzi, B. Jansik, H. J. Aa. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawłowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. Rybkin, P. Salek, C. C. M. Samson, A. Sánchez de Merás, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. Sneskov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. Watson, D. J. Wilson, M. Ziolkowski, and H. Ågren, *The DALTON quantum chemistry program system*, *WIREs Comput. Mol. Sci.* 4, 269 (2014).

- 15 S. Bruun-Ghalbia, S. P. A. Sauer, J. Oddershede, and J. R. Sabin, Eur. Phys. J. D 60, 71 (2010); S. P. A. Sauer, J. Oddershede, and J. R. Sabin, J. Phys. Chem. C 114, 20335 (2010); S. P. A. Sauer, J. Oddershede, and J. R. Sabin, Adv. Quantum Chem. 71, 29 (2015).
- 16 S. P. A. Sauer, I. Ul Haq, J. R. Sabin, J. Oddershede, O. Christiansen, and S. Coriani, Mol. Phys. 112, 751 (2014).
- 17 T. H. Dunning, J. Chem. Phys. 90, 1007 (1989); R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. 96, 6796 (1992); D. E. Woon and T. H. Dunning, J. Chem. Phys. 98, 1358 (1993); D. E. Woon and T. H. Dunning, J. Chem. Phys. 100, 2975 (1994); D. E. Woon and T. H. Dunning, J. Chem. Phys. 103, 4572 (1995).
- 18 W. Thomas, Naturwissenschaften 13, 627 (1925); F. Reiche and W. Thomas, Z. Phys. 34, 510 (1925); W. Kuhn, Z. Phys. 33, 408 (1925).
- 19 P. Jørgensen and J. Oddershede, J. Chem. Phys. 78, 1898 (1983).
- 20 S. P. A. Sauer, J. Oddershede, and J. R. Sabin, Adv. Quantum Chem. 71, 29 (2015).
- 21 M. Inokuti, *Moments of the Oscillator Strength Distribution and Some Associated Quantities for the Hydrogen Atom*. Argonne National Laboratory Report ANL 6769, 7 (1963).
- 22 M. Inokuti, Rev. Mod. Phys. 43, 297 (1971).
- 23 E. S. Nielsen, P. Jørgensen, and J. Oddershede, J. Chem. Phys. 73, 6238 (1980).
- 24 J. Oddershede and J. R. Sabin, Phys. Rev. A 39, 5565 (1989).
- 25 J. Oddershede and J. R. Sabin, Nucl. Instr. Meth. Phys. Res. B 48, 34 (1990).
- 26 J. C. Slater, Phys. Rev. 36, 57 (1930).
- 27 P. B. Parks, G. A. Gerdin, L. L. Vahala, and A. G. Elcashlan, Nucl. Fusion 34, 417 (1994).