Ionization Energy and Level Shifts of Multiply Charged Ions in Nonideal Plasmas

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The Bethe-Salpeter equation for plasmas containing ions with higher charges is solved by perturbation methods. The lowering of the ionization energy as well as the energy level shifts due to nonideality effects are calculated. It is shown that multiply charged ions lead to an essential amplification of nonideality effects. An estimate for the modification of transition rates is given.

Key words: Multiply charged ions, Ionization energy, Level shift, Lyman series, Ionization kinetics.

1. Introduction

Plasmas with multiply charged ions are of great importance for many applications as, e.g., near-electrode phenomena in arcs, pulsed high-current discharges, plasmas produced by wire explosions, shock fronts, high-intensity lasers and ion beams. Let us mention also that the development of X-ray lasers is closely connected with the behaviour of highly ionized plasmas of heavy elements. Most of the existing studies of nonideality effects in many-component plasmas have been restricted so far to ions carrying one protonic charge only [1–4]. There are, however, also first approaches to develop a theory for plasma systems with arbitrary charges [5–9].

Considering plasmas which contain ions of charge $(+Z\varepsilon)$, we are expecting that the interactions of these ions increase with Z. Therefore multiply charged ions may give rise to strong nonideality effects [7, 8]. Here we are especially concerned with the influence of nonideality on the ionization energy, which is a key quantity for the ionization kinetics [10, 11], and with the shifts of the energy levels, which are fundamental for the problems of optical transitions [12, 13].

2. The Model

Let us consider a non-degenerate plasma which consists of electrons with the total number density n_e carrying the charges $(-\varepsilon)$ and one species of nuclei (charge: $+Z\varepsilon$) with the number density n_n. From electroneutrality follows

$$n_e = Z\, n_n\,. \tag{1}$$

Introducing the number densities of free electrons n_e^*, singly charged ions n_1, doubly charged ions n_2 etc., as well as the number densities of free bare nuclei n_Z and the number density of neutral atoms n_0 we get the balance equations

$$n_e = \sum_{z=0}^{Z-1} (Z-z)\, n_z\,; \quad n_n = \sum_{z=0}^{Z} n_z\,. \tag{2}$$

Regarding the neutral atoms and their ions in different levels of ionization as new species we should have to develop a many-body theory of a multicomponent plasma consisting of atoms, electrons and Z species of ions. Within this chemical picture of the system one needs as an input into the theory the interaction potentials between all the species. The interaction between electrons and ions with arbitrary inner shell configurations (parent configurations) were recently determined by Rogers et al. [14]. The interactions between the ions, however, remain to be an open problem.

For the sake of simplicity and in order to study the main nonideality effects which are due to $Z+1$ we restrict our considerations to the non-degenerate case

$$n_e \Lambda_e^3 < 1\,; \quad \Lambda_e = \frac{h}{(2\pi\, m_e\, k_B T)^{1/2}} \tag{3}$$

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and to the temperature-density region where the number densities of atoms n_0 and of all ions except one

$$n_z \ll n_e^*; \quad z=0, 1, 2, \ldots, Z-2, \tag{4}$$

are negligible.

The remaining species of ions is hydrogenlike. It consists of a Z-fold charged nucleus and one electron. Energies and wave functions for the bound and scattering states of this ion can easily be obtained from the hydrogen data by a simple scaling procedure

$$e_{\text{proton}} \rightarrow Z\varepsilon . \tag{5}$$

Under this conditions the balance equations (2) have the form

$$n_e \approx n_e^* + n_{Z-1}; \quad n_n \approx n_{Z-1} + n_Z . \tag{6}$$

So the system we shall study is mainly composed of electrons, nuclei and hydrogenlike ions. We adopt the physical picture as the starting point. That means the ions will be regarded as bound states of nuclei and electrons. All interactions are of Coulomb type.

The first question one has to answer is the shift of bound state energies and of the continuum edge as function of density and temperature. The key quantity, which governs the two-particle spectrum and their damping rate is the spectral function of the two-particle Green's function in the s-channel.

3. The Bethe-Salpeter Equation

A theory of two-particle states taking into account the surrounding medium was derived in [3, 4, 15]. The approach leads to an effective wave equation which includes

(i) dynamical self-energy,
(ii) exchange self-energy,
(iii) dynamical screened Coulomb interaction,
(iv) phase space occupation,

$$\begin{aligned}\{\varepsilon_e(p_1)+\varepsilon_n(p_2)-\tilde{E}\}\,\Psi_{en}(p_1\, p_2\, \tilde{E}) &\\ +\sum_q V_{en}(q)\Psi_{en}(p_1-q,\, p_2+q,\, \tilde{E}) &\\ =\sum_q H_{en}^{pl}(p_1\, p_2; p_1-q\, p_2+q; \omega)\,\Psi_{en}(p_1-q;\, p_2+q;\, \tilde{E}).&\end{aligned} \tag{7}$$

Here the ε_e, ε_n denote the kinetic energies of bare electrons and nuclei

$$\varepsilon_e = \frac{p_1^2}{2m_e}; \quad \varepsilon_n = \frac{p_2^2}{2m_n}. \tag{8}$$

The potential V_{en} is the bare electron-nucleus potential

$$V_{en}(q) = -\frac{4\pi Z\varepsilon^2}{q^2}, \tag{9}$$

and H_{en}^{pl} is the plasma-operator, taking account of the effects mentioned above,

$$\begin{aligned}H_{en}^{pl}&(p_1\, p_2; p_1-q\, p_2+q; \omega)\\ &= \Delta_{en}(p_1\, p_2; \omega)\,\delta_{q,0} + \Delta V_{en}^{eff}(p_1\, p_2; q, \omega).\end{aligned} \tag{10}$$

Here in Δ_{en} are condensed the self energy contributions (i) and (ii), whereas in ΔV_{en}^{eff} we have the effects (iii) and (iv). H_{en}^{pl} is an hermitian operator and depends on the real frequency ω as a parameter. Therefore the energies $\tilde{E}$ also depend on ω. The two-particle energies as the singularities of the spectral function are solutions of the dispersion equation

$$\omega = \tilde{E}_n(\omega). \tag{11}$$

Explicit expressions for Δ_{en} and ΔV_{en}^{eff} in different approximations can be found in [15]. There the substitution (5) has to be performed.

In a very rough simplification of H_{en}^{pl}, neglecting Pauli effects and replacing the dynamic interaction ΔV_{en}^{eff} by the corresponding static Debye limit, one obtains in perturbation theory for the energies of the hydrogenlike ions

$$\tilde{E}_{kl}^{(Z-1)} = E_k^{(Z-1)} + \Delta_e + \Delta_n + \Delta_{kl}^{(Z-1)}. \tag{12}$$

The three main contributions to the unperturbed energy $E_k^{(Z-1)}$ are the self-energies of electrons Δ_e, of nuclei Δ_n and the Debye shift $\Delta_{kl}^{(Z-1)}$. In Debye approximation we have

$$\Delta_e \approx -\frac{\varepsilon^2 \varkappa}{2}; \quad \Delta_n \approx -\frac{Z^2\varepsilon^2\varkappa}{2}. \tag{13}$$

More complete approximations of the self-energies by Padé approximations for the chemical potentials may be found elsewhere [2, 10, 16, 17].

The Debye shift of the energy level k is estimated here as the expectation value of the difference between Coulomb potential and Debye potential,

$$\Delta_{kl}^{(Z-1)} = \langle \Delta V_{en}^{eff}(E_k^{(Z-1)})\rangle_{kl} \approx Z\varepsilon^2 \langle r^{-1} - r^{-1} e^{-\varkappa r}\rangle_{kl}. \tag{14}$$

Here $\varkappa$ is the inverse Debye screening radius

$$r_D^{-1} = \varkappa = \left\{4\pi\varepsilon^2 \left[n_e^* + \sum_{z=1}^{Z} n_z z^2\right] \Big/ k_B T\right\}^{1/2}. \tag{15}$$

In order to obtain an analytical expression for $\Delta_{kl}^{(Z-1)}$ we expand (14) in different temperature density regions

$$\Delta_{kl}^{(Z-1)} = Z\,\varepsilon^2 \begin{cases} \varkappa - \frac{1}{2}\varkappa^2 \langle r\rangle_{kl} + \frac{1}{6}\varkappa^3 \langle r^2\rangle_{kl} + \ldots; & \varkappa a_B \ll 1, \\ \langle r^{-1}\rangle_{kl} + \ldots; & \varkappa a_B \gg 1. \end{cases} \tag{16}$$

Here a_B is the Bohr radius of the hydrogenlike ion.

$$E_k^{(Z-1)} = -\frac{Z\,\varepsilon^2}{2\,a_B\,k^2}; \quad a_B = \frac{\hbar^2}{Z\,\varepsilon^2\,\mu_{en}}; \quad \mu_{en}^{-1} = m_e^{-1} + m_n^{-1}. \tag{17}$$

The $\langle r^n\rangle_{kl}$ are the expectation values of r^n for the orbit $\{k\,l\}$ corresponding to the eigenstate $|k\,l\rangle$. For hydrogenlike ions one finds [18]

$$\langle r^{-1}\rangle_{kl} = \frac{1}{k^2\,a_B}; \quad \langle r\rangle_{kl} = \tfrac{1}{2}\,[3\,k^2 - l(l+1)]\,a_B\,,$$
$$\langle r^2\rangle_{kl} = \tfrac{1}{2}\,[5\,k^2 + 1 - 3\,l(l+1)]\,k^2\,a_B^2\,. \tag{18}$$

On the basis of these results we will discuss the lowering of the ionization energy and level shifts in more detail.

With the expressions (18) we arrive at

$$a_{kl}^Z = \frac{a_B}{48\,k^2}\,\{7\,k^4 - 4\,k^2 - 6\,k^2\,l(l+1) + 3\,l^2(l+1)^2\},$$
$$b_{kl}^Z = \frac{a_B}{48\,k^2}\,\{29\,k^4 + 4\,k^2 - 6\,k^2\,l(l+1) - 3\,l^2(l+1)^2\},$$
$$c_{kl}^Z = \frac{a_B^2}{48}\,\{7\,k^4 - 4\,k^2 - 6\,k^2\,l(l+1) + 3\,l^2(l+1)^2\}. \tag{22}$$

Thus we obtain for the spectral line shift of the hydrogenlike ions

$$\Delta E_{kl\to k'l'} = \Delta_{kl}^{(Z-1)} - \Delta_{k'l'}^{(Z-1)} \tag{23}$$
$$= Z\,\varepsilon^2\,\varkappa \left\{ \frac{1 + a_{kl}^Z\,\varkappa}{1 + b_{kl}^Z\,\varkappa + c_{kl}^Z\,\varkappa^2} - \frac{1 + a_{k'l'}^Z\,\varkappa}{1 + b_{k'l'}^Z\,\varkappa + c_{k'l'}^Z\,\varkappa^2} \right\}.$$

For the Lyman series, e.g. ($k' = 1$, $l' = 0$, $l = 1$, $k = 2, 3, \ldots$),

$$\Delta E_{kp\to 1s} = Z\,\varepsilon^2\,\varkappa \left\{ \frac{48\,k^2 + (\varkappa a_B)\,[7\,k^4 - 16\,k^2 + 12]}{48\,k^2 + (\varkappa a_B)[29\,k^4 - 8\,k^2 - 12] + (\varkappa a_B)^2\,[7\,k^4 - 16\,k^2 + 12]} - \frac{48 + 3(\varkappa a_B)}{48 + 33(\varkappa a_B) + 3(\varkappa a_B)^2} \right\}.$$

4. Discussion of the Ionization Energy, Level Shifts and Spectral Line Shifts of Hydrogenlike Ions

From our estimate follows in the lowest approximation for the ground state energy ($\varkappa a_B \ll 1$)

$$\tilde{E}_{1s}^{(Z-1)} = E_{1s}^{(Z-1)} - \tfrac{1}{2}\,(Z-1)^2\,\varepsilon^2\,\varkappa\,. \tag{19}$$

This result was already obtained in [19]. In the case of a symmetric plasma ($Z = 1$), the ground state energy in this approximation remains unchanged. Further, (19) is in agreement with the calculations of Kudrin [9]. We may conclude therefore that our basic assumption (12)–(14) is a reasonable approximation.

Let us consider now the excited states. Then the parameter $\varkappa\,\langle r^n\rangle_{kl}$ is large and can not be neglected. For estimate let us use the Padé approximation

$$\Delta_{kl}^{(Z-1)} = Z\,\varepsilon^2\,\varkappa\,\frac{1 + a_{kl}^Z\,\varkappa}{1 + b_{kl}^Z\,\varkappa + c_{kl}^Z\,\varkappa^2}\,, \tag{20}$$

where the Páde coefficients are given by

$$a_{kl}^Z = \{\tfrac{1}{4}\,\langle r\rangle_{kl}^2 - \tfrac{1}{6}\,\langle r^2\rangle_{kl}\}\,\langle r^{-1}\rangle_{kl}\,,$$
$$b_{kl}^Z = \tfrac{1}{2}\,\langle r\rangle_{kl} - a_{kl}^Z\,,$$
$$c_{kl}^Z = \frac{a_{kl}^Z}{\langle r^{-1}\rangle_{kl}}\,. \tag{21}$$

For the continuum edge, V_{en} and $\Delta V_{en}^{\mathrm{eff}}(\omega)$ in the effective wave equation (7) can be neglected. It means that we observe a strong lowering of the continuum edge due to self-energy effects Δ_{en}.

$$\tilde{E}_{\mathrm{scat.}}^{(Z-1)}(p_1 = p_2 = 0) = \Delta_e + \Delta_n \approx -\frac{(1 + Z^2)\,\varepsilon^2\,\varkappa}{2}\,. \tag{25}$$

Here we observe a strong dependence on density, in contrast to the ground state level. There is no compensation even for symmetric plasmas.

The effective ionization energy is the gap between the ground state and the continuum level. Corresponding to (12) and (25) this gap is given by

$$I^{(Z-1)} = |E_{1s}^{(Z-1)}| - \Delta_{1s}^{(Z-1)} \tag{26}$$

with

$$\Delta_{1s}^{(Z-1)} = Z\,\varepsilon^2\,\varkappa \left\{ \frac{48 + 3\,(\varkappa\,a_B)}{48 + 33(\varkappa\,a_B) + 3(\varkappa\,a_B)^2} \right\}.$$

This way we observe that the lowering of ionization energy increases with Z.

We suppose for a moment that our approximation of vanishing densities n_1, n_2 for singly ionized, doubly ionized ions etc. could be removed regarding those ions as complexes interacting by pure Coulomb potentials, which to a wide extent seems to be a good approximation. The short range part of their interaction potential decreases rapidly and becomes therefore important at high densities [14]. These ions carry a net protonic charge ε, 2ε etc. Thus for these ions the effective Z is 1, 2, etc. In such a mixture of singly, doubly and multiply ionized atoms due to (26) those with the higher ionization level display a stronger lowering of the ionization energy. Multiply charged ions feel a stronger influence of nonideality effects than singly charged ions [8].

The ionization energy of an ion being in the quantum state $|kl\rangle$ may be in the same approximation represented by

$$I_{kl}^{(Z-1)} = |E_{kl}^{(Z-1)}| - \Delta_{kl}^{(Z-1)}. \tag{27}$$

We observe that higher levels merge into the continuum at lower densities than the ground state.

Let us note that the effective ionization energy is a quantity of primary physical interst since it determines many physical quantities. One example will be demonstrated in the next section.

5. Application to Ionization Kinetics

Again extending a little bit the model of Sect. 2 as we have done in the previous section, let us assume that the rate equations for the electron kinetics have the shape [7, 10, 11, 20]

$$\dot{n}_e^* = \sum_{z=0}^{Z-1} [\alpha_z^R n_z + \alpha_z n_e^* n_z - \beta_z^R n_e^* n_{z+1} - \beta_z (n_e^*)^2 n_{z+1}]. \tag{28}$$

The coefficients describe the following processes:

α_z^R ionization by radiation,
α_z ionization by electron collision,
β_z^R radiation recombination,
β_z three-particle recombination.

For physical reasons let us assume now that in a dense thermal plasma the ionization coefficients show an Eyring-type exponential dependence on the ionization energy, e.g.

$$\alpha_{Z-1} = \alpha_{0,Z-1} \exp[-I^{(Z-1)}/k_B T]. \tag{29}$$

In nonideal plasmas therefore these coefficients show a strong density dependence due to the change of the effective ionization energy. Taking (26) into account, we shall assume that the ideal expression is modified in the following way [7, 8]:

$$f_\alpha^z = \frac{\alpha_{z-1}}{\alpha_{z-1}^{id}} = \frac{\alpha_{z-1}^R}{\alpha_{z-1}^{R,id}} = \exp[\Delta_{1s}^{(z-1)}/k_B T]$$
$$= \exp\left[\frac{z\varepsilon^2 \varkappa (1 + a_{1s}^{(z)} \varkappa)/k_B T}{1 + b_{1s}^z \varkappa + c_{1s}^z \varkappa^2}\right]. \tag{30}$$

On the other hand, we assume that the recombination coefficients show only a weak dependence on the density, which may be neglected in first approximation. These assumptions are consistent with the quantum-statistical results of Klimontovich [13] and Bornath, Schlanges and Kremp [10, 11] for hydrogen. Further, these assumptions are consistent with the mass action law for nonideal plasmas, which should be fulfilled in the static case. For all these reasons we shall use the approximation

$$\frac{\beta_z}{\beta_z^{id}} = \frac{\beta_z^R}{\beta_z^{R,id}} = 1. \tag{31}$$

In this way the rate equations for nonideal plasmas with multiply charged ions are completely specified.

So far we have considered the bound electrons only in total, i.e. we did not specify the different possible states of excitation. A more complete picture has to count separately the electrons being in the k-th quantum state of the ion with z charges ($z=0$ to $Z-1$). Denoting the number density of this population by n_k^z, we have the balance for the electrons

$$n_e = n_e^* + \sum_{k,z} n_k^z. \tag{32}$$

Here again n_e^* denotes the number density of free electrons. In this more complete description the ionization and recombination coefficients depend on two indices denoting the source and the target state of the transition. For an estimate of the nonideality effects let us assume again that the up-hill transitions $k \to l$ ($E_l > E_k$) contain Eyring-type exponents in the rate coefficients and the down-hill transitions are identical with the ideal ones. With this assumption we get the estimate

$$\frac{\alpha_{z-1}(k\to l)}{\alpha_{z-1}^{id}(k\to l)} = \frac{\alpha_{z-1}^R(k\to l)}{\alpha_{z-1}^{R,id}(k\to l)} = \exp\left[\frac{\Delta_k^{(z-1)} - \Delta_l^{(z-1)}}{k_B T}\right],$$
$$\frac{\beta_{z-1}^R(k\to l)}{\beta_{z-1}^{R,id}(k\to l)} = \frac{\beta_{z-1}(k\to l)}{\beta_{z-1}^{id}(k\to l)} = 1. \tag{33}$$

Let us underline, however, that the rate coefficients given here may be considered only as estimates. In a more complete theory, beside the level shifts also nonideal contributions to the scattering processes have to be taken into account.

6. Conclusions

The existence of multiply charged ions in plasmas strongly influences the effects of nonideality. We concentrated on the study of the effective ionization energy and level shifts and their influence on transition phenomena. The most interesting result is, that nonideality favours the production of higher excited states and of multiply charged ions which by their strong Coulombic forces increase the nonideality. This may lead to feedback loops which make the production of strongly ionized plasmas of the heavier elements much more favourable than one would expect from the ideal laws.

Without doubt, precise experimental investigations of the ionization rates in dense plasmas of the heavier elements would be extremely useful in order to solve some of the open questions. Theoretical questions which refer to more realistic interactions and the role of short range parts of them are left to a forthcoming paper.

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