

SHIFT OF ATOMIC ENERGY LEVELS IN A PLASMA

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A diagram technique is used for analyzing level shifts in single-electron atoms in an equilibrium plasma at a finite temperature. The level shifts are computed to first and second order in the coupling constant $e^2/2aT$ (a is the Bohr radius). Debye shielding is taken into account by summing over diagrams. At high temperatures ($T \gtrsim 10^6$ K) the shift is determined by the electron-electron exchange interaction and increases as $T^{1/2}$. The problem of calculating level widths is discussed.

1. INTRODUCTION

IN recent years considerable progress has been made^[1] in analyses of the effect of a plasma on the spectra of atoms in the plasma; these analyses consider effects due to electrons and ions by a combination of collision and statistical methods, using both quantum mechanical and classical descriptions; the correlation between charged particles has also been included. Nonetheless, the problem of describing these effects by means of a unified point of view remains unsolved. The application of quantum field theory techniques in quantum statistics (the Matsubara technique^[2] and the further development of the Green's function technique^[3-5]) open the possibility of a new approach to the problem. In this case one can formulate a quantum description of the entire plasma and then take account of correlation with the atoms.

Using the point of view of field theory we shall consider the state of an electron in the plasma in terms of single-electron excitations. These excitations will correspond to bound electron states in the atom if these states become single-electron states in an isolated atom as the charged-particle density of the plasma approaches zero. To use this approach we isolate one of the ions and consider the entire plasma in the Coulomb field of this ion. The energy changes of the single-electron excitations then represent shifts of the atomic energy levels in the plasma while their imaginary parts represent the widths of the corresponding levels.

2. SINGLE-ELECTRON EXCITATIONS

We compute the energy level shifts for single-electron atoms in an equilibrium plasma at tem-

perature $T = \beta^{-1}$. The entire plasma is considered in the "external" field due to an isolated ion, which is assumed to be fixed. The kinetic energy of the electrons and ions is included in the unperturbed plasma Hamiltonian H_0 while the interaction Hamiltonian is written in the form

$$H_1 = H_{ee} + H_{ei} + H_{ii} + V_e + V_i; \tag{1}$$

$$H_{ee} = \int dx dy \psi^+(x) \psi^+(y) u(x-y) \psi(y) \psi(x),$$

$$V_e = \int dx \psi^+(x) \psi(x) V(x),$$

$$H_{ii} = Z^2 \int dx dy \varphi^+(x) \varphi^+(y) u(x-y) \varphi(y) \varphi(x),$$

$$V_i = -Z \int dx \varphi^+(x) \varphi(x) V(x),$$

$$H_{ei} = -Z \int dx dy \psi^+(x) \psi(x) u(x-y) \varphi^+(y) \varphi(y). \tag{2}$$

Here, ψ^+ and ψ are electron creation and annihilation operators while φ^+ and φ are the same for ions in the temperature representation of the interaction, $u(x-y) = u(\mathbf{x}-\mathbf{y}) \delta(x^0-y^0)$ is the potential energy of the interaction for an electron pair, $V(\mathbf{x})$ is the potential energy of an electron in the external field, Z is the charge of nucleus* and the subscripts e and i refer to electrons and ions respectively. The integration over the 4-vector \mathbf{x} is carried out over the entire three-dimensional space of the vector \mathbf{x} and over the interval $(0, \beta)$ of the temperature variable x^0 .

It follows from the spectral representation of the single-particle Green's function^[3,5] that its poles give the energy spectrum of the single-particle excitations. We consider the single-electron temperature Green's function^[2,4]

$$G(x, y) = \langle S(\beta) \rangle^{-1} \langle T \{ \psi^+(x) \psi(y) S(\beta) \} \rangle, \tag{3}$$

*When $Z > 1$ we assume that all perturbing ions are completely ionized.

where $S(\beta)$ is the Matsubara S-matrix, the T ordering is carried out over the temperature variable, while the averaging is taken by means of the density matrix of the noninteracting particles $\exp\{\Omega + \mu N - H_0\beta\}$. As is well known, the Green's function G satisfies the Dyson equation

$$G(x, y) = S(x - y) + \int dx' dy' S(x - x') \Sigma^*(x', y') G(y', y), \quad (4)$$

where $S(x - y)$ is the Green's function for the free electron

$$\left(\frac{\partial}{\partial x^0} + \mu + \frac{1}{2m} \Delta_x\right) S(x - y) = \delta(x - y), \quad (5)$$

while Σ^* is the compact self-energy part. The quantity Σ^* represents the sum of all compact diagrams with two external electron lines. In Fig. 1 we show these diagrams for first (1-4) and second (in H_1) order perturbation theory. The single solid line corresponds to the electron,

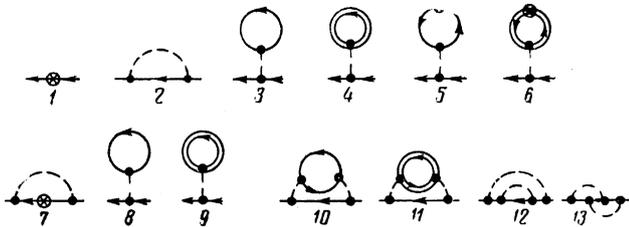


FIG. 1

the double solid line corresponds to the ion, the dashed line corresponds to the Coulomb interaction and the starred line corresponds to the external field. Using Eq. (5) we can obviously rewrite Eq. (4) in the form

$$\left(\frac{\partial}{\partial x^0} + \mu + \frac{1}{2m} \Delta_x\right) G(x - y) - \int dz \Sigma^*(x, z) G(z, y) = \delta(x - y). \quad (6)$$

The Green's function is an antiperiodic function of the difference $x^0 - y^0$ [4,5]; hence the integral in Eq. (6) must be the same function of this difference. This requirement is satisfied by two functional forms of the dependence of $\Sigma^*(x, z)$ on $x^0 - z^0$: a delta function and an antiperiodic function. All diagrams in Fig. 1 except for 10, 11, and 13 refer to the first function; 10, 11, and 13 refer to the second.

We remove from Σ^* the term corresponding to diagram 1 of Fig. 1, which is independent of plasma density, and introduce the mass operator M defined by $\Sigma^*(x, z) = V(x) \delta(x - z) + M(x, z)$. Then, from Eq. (6) we obtain the equation

$$\left[\frac{\partial}{\partial x^0} + \mu + \frac{1}{2m} \Delta_x - V(x)\right] G(x, y) - \int dz M(x, z) G(z, y) = \delta(x - y). \quad (7)$$

We let the density of charged particles in the plasma approach zero so that the mass operator approaches zero and (7) becomes an equation for the Green's function of the single-electron atom. Thus, the mass operator in (7) takes account of the effect of the plasma on the atom.

It is well known [4,5] that we can carry out a Fourier transformation over "time" x^0 within the temperature diagram technique:

$$G(\omega_n) = \frac{1}{2} \int_{-\beta}^{\beta} e^{i\omega_n x^0} G(x_0) dx_0, \quad (8)$$

where $\omega_n = \pi(2n + 1)/\beta$ for electrons. In the frequency representation Eq. (7) is

$$\left[-i\omega_n + \mu + \frac{1}{2m} \Delta_x - V(x)\right] G(x, y, \omega_n) - \int dz M(x, z, \omega_n) G(z, y, \omega_n) = \delta(x - y)$$

or, in operator form*

$$G^{-1}(\omega_n) = -i\omega_n + \mu + \Delta_x/2m - V(x) - M(\omega_n).$$

The poles of G (zeros of G^{-1}) in the complex plane $E = -i\omega_n + \mu$ determine the spectrum of the energy of single electron excitations of the system; thus, the determination of this spectrum reduces to solution of the equation

$$\left[-\frac{1}{2m} \Delta_x + V(x) + M(\omega_n = iE_\nu - i\mu)\right] \chi_\nu = E_\nu \chi_\nu. \quad (9)$$

Using the perturbation method, we find the zeroth approximations (in M) of the energy levels E_ν^0 and the eigenfunctions χ_ν^0 of the single-electron atom; in the first approximation

$$E_\nu = E_\nu^0 + M_{\nu\nu}(\omega_n = iE_\nu^0 - i\mu), \quad (10)$$

where $M_{\nu\nu}$ is the matrix element of M in the basis χ_ν^0 . This matrix element gives the shift of the energy level for the state χ_ν^0 .

3. MASS OPERATOR

In the first approximation we obtain for $M^{(1)}$ three terms, corresponding to diagrams 2, 3 and 4 in Fig. 1. Diagram 2, which describes the exchange interaction between electrons, corresponds to the matrix

*For the delta-function terms in $x^0 - y^0$ we take $M(x, y, \omega_n)$ to mean the multiplier for $\delta(x^0 - y^0)$ in $M(x, y)$.

$$M_2^{(1)}(x, y) = S(x - y) u(x - y) = \delta(x^0 - y^0) N e^2 |x - y|^{-1} \exp[-(x - y)^2 / 4\lambda^2], \tag{11}$$

where $\lambda = (\beta/2m)^{1/2}$.

Diagrams 3 and 4 correspond to the matrices

$$M_3^{(1)}(x, y) = \delta(x - y) \int dz u(x - z) N, \\ M_4^{(1)}(x, y) = -\delta(x - y) \int dz u(x - z) Z N_i,$$

which describe the interaction of the atomic electron with the self-consistent field of the electrons and ions (mean densities M and N_i). Each of these integrals diverges separately; however they balance each other in a quasi-neutral plasma ($N = ZN_i$). In the second approximation there are three pairs of compensating diagrams; these are not shown in Fig. 1.

In the second approximation, we first must consider diagrams 5, 6, 8, 9, 10, and 11, which lead to divergent integrals and make the largest contribution to the level shift. Diagram 5, which describes the interaction of the atomic electron with the plasma electrons (which are polarized by the field of the nucleus), corresponds to the matrix

$$M_5^{(2)}(x, y) = \delta(x - y) (2\pi)^{-3} \int dk e^{-ikx} P_e^{(2)}(k, 0) V(k) u(k), \tag{12}$$

where $u(k) = 4\pi e^2 k^{-2}$.

Diagram 10, which describes the exchange interaction (taking account of the polarization of the plasma electrons), corresponds to a matrix of the following form in the momentum-frequency representation:

$$M_{10}^{(2)}(p, \omega_n) = 2(2\pi)^{-3} \beta^{-1} \times \sum_m \int dk S(p - k, \omega_{n-m}) P_e^{(2)}(k, \omega_m) u^2(k), \tag{13}$$

where $S(p, \omega_n) = (-i\omega_n + \mu - \epsilon_p)^{-1}$ for odd frequencies while the second-order electron polarization operator is

$$P_e^{(2)}(k, \omega_{2n}) = (2\pi)^{-3} \int dp \frac{(f_p - f_{p-k})(\epsilon_p - \epsilon_{p-k})}{(\epsilon_p - \epsilon_{p-k})^2 + \omega_{2n}^2}$$

and zero for odd frequencies; here, f_p and ϵ_p are the Fermi function and the kinetic energy of an electron with momentum p . For a nondegenerate plasma and zero frequency we have

$$P_e^{(2)}(k, 0) = -N\beta I(\lambda k) \cong -N\beta \left(1 + \frac{1}{2} \lambda^2 k^2\right), \\ I(\xi) = \int_0^1 e^{-\xi^2(1-s^2)/4} ds; \tag{14}$$

for nonvanishing frequencies and small k we have

$$P_e^{(2)}(k, \omega_{2n}) \cong -N\beta 2 \left(\frac{\lambda k}{2\pi n}\right)^2.$$

Diagrams 6 and 11 correspond to the expressions obtained from (12) and (13) when the electron polarization operator is replaced by the ion operator $P_i^{(2)}$. The last is obtained from (14) if N is replaced by N_i and λ by $\kappa\lambda$, where κ^2 is the ratio of electron mass to ion mass.

The integrals in the matrix elements (12) and (13) diverge at small k . In order to avoid this divergence we must take account of the Debye shielding^[2,5,6], that is to say we must consider plasma polarization in all the orders. This can be done by introducing the effective electron interaction potential, obtained by summing the most important polarization diagrams of Fig. 2, containing successively m electron and n ion branches. We replace these branches by the most general compact polarization diagrams; then,



FIG. 2

taking account of the equal and independent contributions of diagrams differing in order of alternation of the electron and ion polarization operators P_e^* and P_i^* we find the effective electron interaction potential:

$$\tilde{u}(k, \omega_s) = u(k, \omega_s) \sum_{m, n=0}^{\infty} \frac{(m+n)!}{m! n!} \times [u(k, \omega_s) P_e^*(k, \omega_s)]^m [Z^2 u(k, \omega_s) P_i^*(k, \omega_s)]^n = u(k, \omega_s) / \{1 - [P_e^*(k, \omega_s) + Z^2 P_i^*(k, \omega_s)] u(k, \omega_s)\}, \tag{15}$$

where $u(k, \omega_s) = u(k)/2$. Thus, $\tilde{u} = u$ for odd frequencies. The effective potential is obtained from Eq. (15) by multiplying by $-Z$ for the electron-ion interaction and by Z^2 for the ion-ion interaction.

The divergences in (12) and (13) can be avoided by taking account in Eq. (15) of the polarization operators P_e^* and P_i^* in the first nonvanishing approximation; they are replaced by $P_e^{(2)}$ from (14) and by $P_i^{(2)}$.

Summation of diagrams of type 5, in which the line of interaction is replaced by the chain of Fig. 2, obviously means that the function $u(k, 0)$ is replaced by $\tilde{u}(k, 0)$ in Eq. (12). Adding a similar summation of diagrams of type 6, we have

$$\begin{aligned}
M_{\text{pol}}(x, y) &= \delta(x-y) 2(2\pi)^{-3} \int dk e^{-ikx} [P_e^{(2)}(k, 0) \\
&+ Z^2 P_i^{(2)}(k, 0)] V(k) \tilde{u}(k, 0) \\
&\cong \delta(x-y) (Ze^2/d) (1 - |x|/2d), \quad (16)
\end{aligned}$$

where $d = [4\pi e^2 (1+Z) N\beta]^{-1/2}$ is the Debye radius.*

In summing the exchange diagrams of type 10 and 11, in which the interaction line is replaced by the chain of Fig. 2, we must take account of the fact that the exchange diagram 2 is a first-order delta function in $x^0 - y^0$, while in all the remaining orders it is antiperiodic. Hence the summation can be carried out conveniently starting with second-order diagrams 10 and 11. This means that in Eq. (13) the quantity $u^2 P_e$ is replaced by $\tilde{u} - u$:

$$\begin{aligned}
M_{\text{exc}}(\mathbf{p}, \omega_{2n+1}) &= \frac{1}{2} (2\pi)^{-3} \beta^{-1} \sum_m \int dk S(\mathbf{p} - \mathbf{k}, \omega_{2n+1-2m}) \\
&\times \frac{[P_e^{(2)}(k, \omega_{2m}) + Z^2 P_i^{(2)}(k, \omega_{2m})] u^2(k)}{1 - {}^{1/2} [P_e^{(2)}(k, \omega_{2m}) + Z^2 P_i^{(2)}(k, \omega_{2m})] u(k)}. \quad (17)
\end{aligned}$$

In this sum the term with $m = 0$ is appreciably greater than the sum of all the remaining terms so that as an approximation we can write

$$\begin{aligned}
M_{\text{exc}}(\mathbf{p}, \omega_{2n+1} = iE_v - i\mu) \\
= \frac{1}{2\pi} e^4 N (1+Z) \int \frac{dk}{k^2 (k^2 + 1/2 a^2) (|E_v| + \epsilon_{p-k})}. \quad (18)
\end{aligned}$$

Diagrams 8 and 9 also give divergent matrix elements and the divergence is again avoided by replacing u by \tilde{u} . Using diagram 8, which describes the interaction of the atomic electron with the plasma electrons (taking account of the interaction between the latter), we obtain the matrix element

$$M_s^{(2)}(x, y) = \delta(x-y) \frac{4\pi}{\sqrt{5}} \frac{e^2}{a} \left(\frac{\lambda}{a}\right)^2 Na^3 \quad (19)$$

(a is the Bohr radius). The matrix element for diagram 9 is obtained from (19) by multiplying by $-\kappa^2$; consequently these do not compensate.

4. LEVEL SHIFT

Equation (10) shows that to find the energy level shift for state χ_{nlm} caused by the plasma we must compute the diagonal element $M(\mathbf{x}, \mathbf{y}, \omega_n = iE_n^0 - i\mu)$ in the basis χ_{nlm} . The shift due to plasma polarization is obtained from (10) and (16):

*This part of the mass operator describes the additional energy of the electron in the Debye field and can be obtained by expansion of the Debye potential $-(Ze^2/r) \exp(-r/d)$ in r/d .

$$\delta E_{nl\text{pol}} = \frac{Ze^2}{a} \left\{ \frac{a}{d} - \frac{1}{4} \left(\frac{a}{d}\right)^2 [3n^2 - l(l+1)] \right\}, \quad (20)$$

and falls off with temperature as $T^{-1/2}$. Diagram 8 corresponds to the level shift obtained from (19):

$$\delta E_{nl} = \frac{4\pi}{\sqrt{5}} \frac{e^2}{a} \left(\frac{\lambda}{a}\right)^2 Na^3, \quad (21)$$

and falls off as T^{-1} with increasing temperature.

To compute the level shift which corresponds to the exchange diagram with the effective potential we note that the matrix element (18) depends on the difference $\mathbf{x} - \mathbf{y}$ in the coordinate representation. Hence it is diagonal in the momentum representation; using the appropriate hydrogen functions, we have from (18)

$$\begin{aligned}
\delta E_{nl\text{exc}} &= \int d\mathbf{p} |\chi_{nlm}(\mathbf{p})|^2 M_{\text{exc}}(\mathbf{p}, \omega_{2n+1} = iE_n^0 - i\mu) = C_{nl} T \frac{a}{d} \\
&= C_{nl} \sqrt{\frac{2aT}{e^2}} \omega_0, \quad (22)
\end{aligned}$$

where ω_0 is the plasmon energy, $\omega_0 = (4\pi e^2 N m^{-1})^{1/2}$. The numerical factor C_{nl} depends on the quantum numbers n and l of the state being considered, being 0.442 for the 1s state, 3.3 for the 2p state, and 3.58 for the 3d state. This shift increases with temperature as $T^{1/2}$.

We now clarify the region of applicability of the results that have been obtained. For this purpose we note that perturbation theory has been used twice in the above—in solving Eq. (9) and in calculating the mass operator. The mass operator in (9) is small because it is proportional to the plasma charge density. The effect of the plasma on the atom is characterized by the number of electrons inside the Bohr orbit, that is, the parameter Na^3 , which is small compared with unity for the gas state. All the mass operator diagrams are proportional to N but the summation carried out above leads to a dependence of the form $M \sim N^{1/2}$ for the largest terms.

We have computed the mass operator above by means of the thermodynamic perturbation theory, i.e., expansion of $S(\beta)$ in H_1 . The largest term in H_1 is the interaction energy of the atomic electron with the nucleus $\sim e^2/a$; thus in the present case the role of the coupling constant is played by the quantity $e^2/2aT = (\lambda/a)^2$, i.e., the ratio of the atomic ionization energy to the thermal energy. We can limit ourselves to the lowest approximations in $S(\beta)$ in the expansion of $e^2/2aT \ll 1$.* Thus, the obtained results apply for high temperatures, (temperatures appreciably greater than 1.5×10^5 K).

*For example, at high temperatures the ratio of level shifts corresponding to diagrams 7 and 2 is of order e^2/aT .

A comparison of the shifts (20) and (22) shows that at high temperatures the important factor is the exchange shift (22), which is a rather large quantity. Thus, when $N = 10^{16} \text{ cm}^{-3}$ and $T = 10^6 \text{ K}$ the $H_{\alpha}(3d \rightarrow 2p)$ line is shifted by 9.4 Å.

The level shifts corresponding to the alpha second-order diagrams not considered in detail above are found to be of order (21) or even smaller at high temperatures and for this reason need not be considered.

The accuracy in the measurement of the shift of a spectral line depends on line width. For this reason we must consider the possibility of computing the broadening of the levels due to the effect of charges in the plasma (Stark broadening). The notion of level width applies only in a continuous energy spectrum which, in the scheme considered above, occurs only when $E_{\nu} > 0$, (unbound electron states). Analytic continuation of the mass operator for computing the level shift of this state makes it necessary to deform the integration contour and gives an imaginary part in δE_{ν} . The latter can arise only in those terms of the mass operator which depend only on frequency ω_{η} , i.e., terms that are not diagonal in $x^0 - y^0$ in the temperature representation. For example, in computing the exchange shift of the energy of the unbound state we find an imaginary part in the zero-frequency term in the sum (17):

$$\begin{aligned} \text{Im } M_{\text{exc}}(\mathbf{p}, \omega_{2n+1}) &= iE_{\nu}^0 - i\mu \\ &= \frac{1+Z}{2} e^4 N \int \frac{dk}{k^2(k^2+d^2)} \delta(E_{\nu} - \epsilon_{\mathbf{p}-\mathbf{k}}) \\ &= \frac{T}{2ap} \ln \frac{1+d^2(p-p_{\nu})^{-2}/2}{1+d^2(p+p_{\nu})^{-2}/2}, \end{aligned} \quad (23)$$

where $p_{\nu} = (2mE_{\nu}^{1/2})$. To compute the level width we must average this expression over unbound electron states.

In the scheme being considered we have a discrete energy spectrum for the bound electron states ($E_{\nu} < 0$). Analytic continuation of the mass operator for these energies leads to an integral which has no singularities along the contour of integration and is thus real. Hence, the width of the negative levels is zero in this scheme. This result is due to our assumption that the nuclei are fixed. Actually, the atomic energy spectrum for bound states is continuous because of the kinetic energy of the atom. Consequently we must take account of the motion of the nuclei in computing the width of the energy levels for the bound states. This approach can be carried out by describing the atom in the plasma by means of the two-particle electron-ion Green's function.

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