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# Formally exact perturbation theory with a model potential as a zeroth approximation I. Transition energies in Fe ions including effects of inner-shell electrons

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**Abstract.** A formally exact perturbation theory with a model potential is developed as a zeroth approximation for atomic systems. A potential of zeroth approximation for a complex system with an arbitrary number of electrons in an open shell and an arbitrary number of vacancies in the core is constructed semiempirically using experimental data for the simplest spectra of one-electron states in an open shell. A field form of perturbation theory is used to calculate energy corrections. Diagrams of the first two orders are considered and an effective summation is performed of diagrams describing major interactions in the system. Energies of all positive Fe ions with open shells  $n = 3$  and 4 and one vacancy (1s, 2s, 2p or 3p) are calculated.

## 1. Introduction

At present, in atomic theory, three calculation methods are most widely used: (i) perturbation theory (expansion in powers of  $1/Z$ ) see, for example, Hylleraas (1930), Tolmachev (1969a, b), Knight (1969), Ivanova and Safronova (1975); (ii) the Hartree–Fock method with different modifications (Hartree 1957, Slater 1960, Jucys and Savukynas 1973); (iii) perturbation theory with a Hartree–Fock zeroth approximation (Kelly 1963). The increase in the number of electrons in the atom leads to an extreme increase in computing difficulties, accompanied by a breakdown in accuracy, while the requirements with regard to accuracy become more rigid. In this connection a model-potential method is used extensively as it simplifies calculations considerably (Bottcher 1971, Yunta *et al* 1974, Bonifacic and Huzinaga 1974, 1975, Bottcher and Dalgarno 1974, Csavinsky and Hucek 1975). In this method the problem is usually solved in a one-particle approximation, with the one-electron potential (imitating a Hartree–Fock potential of the system's core) being parametrized in some way, the parameters being found from experimental one-electron excitation energies. Bottcher and Dalgarno (1974) investigated the analytical dependence of an effective interaction potential of two valence electrons moving in the core field using the polarizability of the latter.

In the present paper, a model one-particle approximation is considered as the zeroth approximation in a formally exact perturbation theory incorporating electron

correlations. This approach allows the determination of the zeroth approximation potential so that it includes a considerable part of the interelectronic interaction and leads to a proper order of excited one-electron levels. It is promising for rapid convergence of the perturbation series. Moreover, perturbation-series structure will be shown to become appreciably simplified by the exact inclusion of one-electron characteristics in the zeroth approximation.

In this paper the contributions of two first-order Feynman diagrams to the energy are studied and an effective summation of diagrams of a definite type is performed in all orders. The particle-hole formalism of the second quantization representation turned out to be especially convenient for the states with inner-shell vacancies considered here.

Strictly speaking, the Hartree-Fock method (the main calculation method in the theory of complex spectra) is not applicable to states with vacancies, as functions of such states must satisfy an infinite number of orthogonality conditions. The known modifications of the Hartree-Fock method give unsatisfactory values of transition energies. Thus, House (1969) calculated the energies of the transitions  $1s-2p$ ,  $1s-3p$  for a great number of ions using the Froese program (Froese 1963). For  $1s-2p$  transitions in Fe ions with ionization degree 1–14, the calculated wavelengths vary within the limits 1.950–1.954 Å, i.e. in the last given figure. Therefore, important information about the spectra under investigation is absent in these results, namely relative positions of lines for similar transitions in ions of different ionization degrees. In real spectra these ions are usually present simultaneously, and the lines of similar transfers overlap to form one line of complex profile, determined by the relative positions of the lines, the transition probabilities and the level populations. The relative positions of the lines are determined by the effective interaction inside the open shell, which may be taken from experimental data for states without vacancies, and by the interaction of outer electrons with the vacancy. The calculation of the latter will receive primary emphasis below.

## 2. Model Hamiltonian

The method is illustrated by the state  $1s2s^22p^63s^1S$ . In the one-particle approximation, chosen as the zeroth one, this state can be represented conveniently as a state with the vacancy  $1s$  and the electron  $3s$  above the core  $1s^22s^22p^6$

$$\Phi = \sum_{\mu\nu} C_{\mu\nu} (-1)^{\frac{1}{2}-\mu} a_{100\mu} a_{300\nu}^{\dagger} \Phi_0 \quad (1)$$

where  $a_{nlms}^{\dagger}$  is the electron creation operator,  $a_{nlms}$  is the electron annihilation operator,  $\Phi_0$  is the core state and the coefficients  $C$ , which provide proper angle symmetry of  $\Phi$ , are in the general case the products of Clebsch-Gordan and fractional parentage coefficients. In the case of an arbitrary state, the nearest state with closed subshells will be taken as a core.

The exact non-relativistic Hamiltonian of a system with any number of outer electrons and vacancies has the form

$$H = \sum_i a_i^{\dagger} a_i \epsilon_i + \left( \sum_{ij} a_i^{\dagger} a_j V_{ij} + \frac{1}{2} \sum_{ijkl} a_i^{\dagger} a_j^{\dagger} a_k a_l V_{ijkl} \right) \quad (2)$$

where  $\epsilon$  is the eigenvalue of the one-electron Hamiltonian with the model potential  $v(r)$ ,

$$V_{ij} = - \int d\mathbf{r} \phi_i^*(\mathbf{r}) [1/r + v(r)] \phi_j(\mathbf{r}) \quad (3)$$

$$V_{ijkl} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_l(\mathbf{r}_1).$$

The model potential will be parametrized as follows (a Coulomb energy unit is used:  $1 \text{ cu} = Z^2 \text{ au} \simeq Z^2 \times 219474 \text{ cm}^{-1}$ ):

$$v(r) = -\frac{1}{Zr} \{Z - N[1 - \exp(-br)(1 + c_1 r + c_2 r^2 + \dots)]\} \quad (4)$$

where  $Z$  is the nuclear charge,  $N$  is the number of electrons in the core and  $b$ ,  $c_1$ ,  $c_2$  are the parameters which can be found from the experimental ionization energies of an atom with one electron above the core in different excited states. The potential, assumed as a perturbation, is bracketed in (2). A convenient iteration procedure for the simultaneous adjustment of several parameters was proposed by Bottcher (1971). In the absence of the required experimental data, one-particle energies could be found from the self-consistency condition of eigenstate energies and the potential parameters according to the scheme proposed by Yunta *et al* (1974). It should be noted that the potential (4) at  $r \rightarrow 0$  and  $r \rightarrow \infty$  coincides with the Hartree core potential.

The empirical potential  $v(r)$  determines a complete set of one-particle states used as a basis for the perturbation theory considered below. Thus the calculation of the energy of the whole atomic system with an arbitrary number of outer electrons and vacancies proceeds in two steps:

- (i) the construction of a model Hamiltonian of zeroth approximation using the experimental data on the simplest spectrum of the outer-electron excitations, and
- (ii) the calculation of corrections of different order within the framework of formally exact Rayleigh-Schrödinger perturbation theory.

### 3. Diagrams for the immediate interaction of a vacancy with the outer electrons

Representing the series of perturbation theory in the form of Feynman diagram contributions, one can interpret physically separate terms in the series and determine a special calculation method to account for various effects of interelectronic interactions.

We shall differentiate three types of diagrams: vacuum ones (without free lines), diagrams with free lines of outer electrons only (directed from the right to the left), and diagrams with free lines of the vacancy (directed from the left to the right). The sum of diagrams of the first type is equal to the core energy; the sum of diagrams of the first and second type equals the energy of the state with the outer electrons above the core, but without vacancies. In all the cases considered, we find this energy by subtracting the ionization energies of the states with the filling shells  $n = 3, 4$  (given by Moore (1949) and in *Ionization Potentials and Ionization Limits*) from the energy of the state  $1s^2 2s^2 2p^6$ , for which reliable theoretical results accounting for relativistic effects are available (Knight 1969, Ivanova and Safronova 1975, Desclaux *et al* 1971).

The contribution of the remaining one-particle diagrams (diagrams with two free lines of the vacancy) equals the energy of the core with one vacancy only, but without valence electrons. The energy of vacancies 1s, 2s, 2p within the core  $1s^2 2s^2 2p^6$ , vacancy 3s within the core  $1s^2 2s^2 2p^6 3s^2$  and vacancy 3p within the core  $1s^2 2s^2 2p^6 3s^2 3p^6$  can be determined almost exactly from the above-mentioned theoretical and experimental data. The change of these energies due to the addition of the next closed subshells will be accounted for as the interaction of the vacancy with electrons of the filling subshell. It should be noted that an error in the determination of the vacancy energy does not affect the mutual positions of levels and transition lines in the same ion and in any two ions with the same core if only the vacancy state is unchanged. Thus, in the first two orders there remain for consideration two- and three-particle diagrams with two free lines of the vacancy, accounting for electron-vacancy interaction.

In the first order two such diagrams are available: a direct one (figure 2(a)) and an exchange one (figure 2(b)). Contributions of these diagrams are expressed through radial integrals

$$R_{\lambda}(n_1 l_1 n_2 l_2 n_4 l_4 n_3 l_3) = \iint dr_1 dr_2 R_{n_1 l_1}(r_1) R_{n_2 l_2}(r_2) U_{\lambda}(r_1 r_2) R_{n_4 l_4}(r_2) R_{n_3 l_3}(r_1) r_1^2 r_2^2 \quad (5)$$

where  $U_{\lambda}(r_1 r_2) = r_{<}^{\lambda} / r_{>}^{\lambda+1}$ ,  $R(r)$  are radial parts of one-electron functions. These contributions have been calculated completely.

Let us consider second-order diagrams. Calculating their contributions, we shall neglect the values which are small compared to the distances between terms of the same configuration. This can be justified by the smallness of the values throughout this paper. Thus it becomes possible in all second-order terms describing electron-vacancy interaction to account for only the spherically symmetric part  $U_0(r_1 r_2)$  of the electron-vacancy interaction  $-1/r_{12}$ . The remaining contribution of the electron-vacancy interaction has an additional smallness parameter  $(R_v/R_a)^2$ , where  $R_v$  is the vacancy radius and  $R_a$  the outer electron orbital radius. Also second-order exchange diagrams are omitted. Thus the contribution of the vacancy interaction with the outer shell to the distances between the terms is taken into account only in first order. The part of this interaction allowed for in second order only shifts all the terms of the same configuration by the same value. This shift is important for the determination of the relative positions of the lines for similar transitions in ions with different ionization degrees.

Among two-particle diagrams of the second order, those with self-energy insets should be pointed out (figure 1). Their contributions are expressed through one-fold sums over virtual states. The method previously described (Ivanov 1976) reduces the calculation of these sums to the solution of an ordinary differential equation.



Figure 1. Self-energy insets.

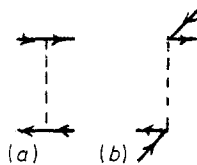


Figure 2. Two-particle first-order diagrams.

For the Hartree-Fock potential, the contributions of diagrams of any order with self-energy insets, as shown by Tolmachev (1969a, b), are exactly compensated. Particular calculations have shown that in our case their contribution is small and so it was neglected.

The contributions of the rest of the second-order diagrams accounted for in the present calculation are also expressed through one-fold sums and can be calculated by a differential equation procedure. However, as will be shown later, there appeared to be a possibility of reducing the procedure to the calculation of the first-order diagrams 2(a) and 2(b) with modified orbitals for the outer electrons and a modified interaction potential for the outer electrons with the vacancy. These modifications allow an effective summation of contributions from diagrams of a definite type in all orders of perturbation theory and, besides, they simplify the calculation appreciably. Let us consider these diagrams.

Figures 3 and 4 show two- and three-particle second-order diagrams representing the immediate (without core polarization) interaction of the vacancy with the filling subshell. The contributions of the diagrams 3(a), 3(b) may be expressed through two-fold sums over the virtual states of electron and vacancy. If in these sums we retain terms without the change in the vacancy state only, then their contribution together with the contribution of first-order diagrams will represent a correction for the energies of outer electrons due to anti-shielding of the core field by the spherically

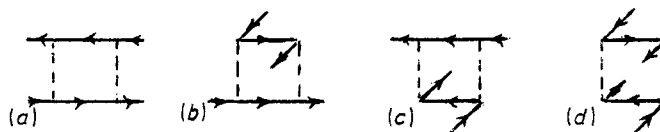


Figure 3. Two-particle second-order diagrams with account of direct vacancy-outer-electron interaction.

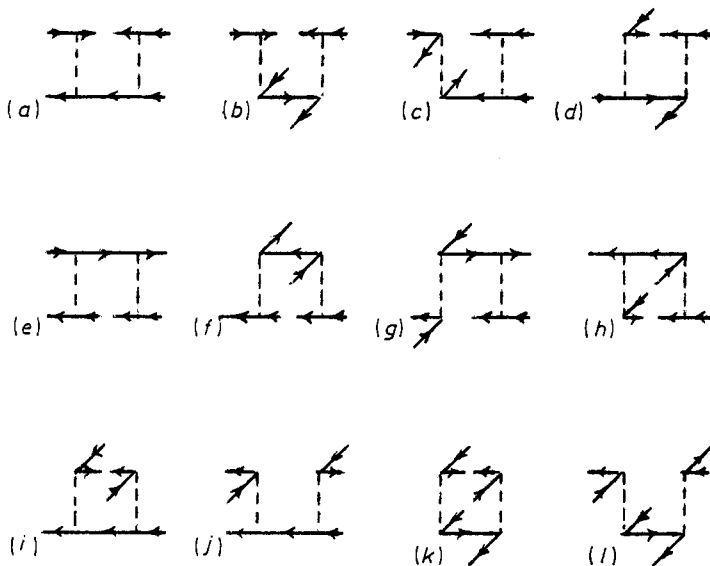


Figure 4. Three-particle second-order diagrams with account of direct vacancy interaction with two outer electrons.

symmetric part of the averaged potential of the vacancy. The influence of the anti-shielding by the vacancy  $n_1l_1$  on the electron  $n_2l_2$  energy may be accounted for effectively by introducing, in the Schrödinger equation for the electron, an additional potential  $-\alpha/r$  such that

$$\alpha \langle n_2l_2 | 1/r | n_2l_2 \rangle = R_0(n_1l_1n_2l_2n_2l_2n_1l_1). \quad (6)$$

The contribution of diagrams 4(a)–4(d) to the energy of the state with outer electron configuration  $nl^k$  may be represented as a correction to the first-order diagrams 2(a), 2(b), which is connected with the correction to the function of an electron state  $nl$  caused by interactions within the outer subshell. To take account of this correction effectively, while determining the radial one-electron function  $R_{nl}$  (but not one-electron energy  $\epsilon_{nl}$ ) we included electrons  $nl^{k-1}$  in the core. For example, in the case of the state  $1s^22s^22p^63s^2$  we found  $R_{3s}$  by numerically solving the radial Schrödinger equation using the one-electron potential (3) with  $Z = 26$ ,  $N = 11$  and parameter  $b$  adjusted so that the eigenenergy be equal to the ionization energy of the state  $1s^22s^22p^63s^2$ .

Contributions of two-particle diagrams shown in figure 3 and three-particle diagrams 4(e)–4(h) which have so far been unaccounted for, may be interpreted as a second-order correction to the vacancy energy in the interaction with the outer electrons. Let us estimate this correction. The averaged potential of the electron  $nl$  at small  $r$  (the region of vacancy localization) may be expanded into a series

$$(1/Z) \int_0^\infty dr' r'^2 R_{nl}^2(r') U_0(rr') = (1/Z) [\langle nl | 1/r | nl \rangle - \frac{1}{6} R_{nl}^2(0) r^2 + \dots]. \quad (7)$$

The first (constant) term in (7) does not contribute to the second-order correction. The contribution of the second (quadratic over  $r$ ) term has the order of smallness  $(R_v/R_a)^4$ . Thus this correction may be neglected. Contributions of three-particle diagrams 4(i)–4(l), representing a second-order correction to the electron energy due to exchange electron–vacancy interaction, are also omitted.

#### 4. Core polarization

This section deals with two-particle diagrams which take into account vacancy interaction with a valence electron through the core (figure 5). These second-order diagrams have been shown by calculations to be the main contributions in the case

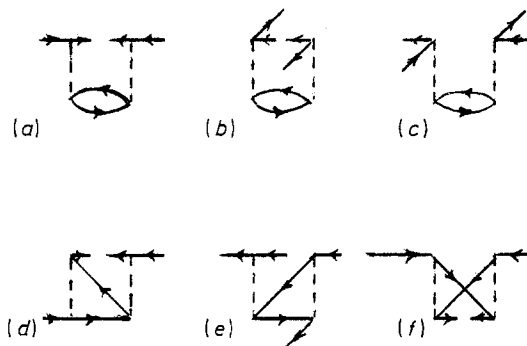


Figure 5. Second-order diagrams with account of core polarization.

of the filling shell  $n = 3$ . Here we restricted ourselves to diagram 4(a) only, the other diagrams unaccounted for in the present calculation representing the influence of exchange effects on core polarization. It should be noted, however, that the method described below may be generalized also for the calculation of contributions from exchange diagrams and contributions from higher harmonics of the Coulomb potential.

Note that the contribution from diagrams 5(a), 5(b), 5(c), to the state energy may be represented as a correction to the contributions from first-order diagrams 2(a), 2(b), which is due to an additional electron–vacancy interaction by means of a potential

$$\tilde{v}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{Z^2} \sum_{i \in g, j \in f} \frac{1}{\epsilon_i - \epsilon_j} \left( \int d\mathbf{r}'_1 \phi_i^*(\mathbf{r}'_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}'_1|} \phi_j(\mathbf{r}'_1) \right) \left( \int d\mathbf{r}'_2 \phi_j^*(\mathbf{r}'_2) \frac{1}{|\mathbf{r}_2 - \mathbf{r}'_2|} \phi_i(\mathbf{r}'_2) \right) \quad (8)$$

where  $\epsilon$  are one-electron energies and  $f, g$  are the occupied and unoccupied core states respectively. Thus it follows from the results of §§2–4 that the initial multi-electron problem with accuracy up to second-order perturbation theory reduces to the problem of the motion of the electrons of the filling shell and one quasi-particle (vacancy) only. For example, the problem of the state  $1s2s^22p^63s$  reduces to the problem of electron  $3s$  and vacancy  $1s$ . The core influences only the one-particle potential, determines regions of summation over the virtual states in the second-order diagrams and also modifies the interaction potential (correction  $\tilde{v}(\mathbf{r}_1, \mathbf{r}_2)$ ).

The contribution of the diagram 5(a) may be interpreted also as a shift of the outer-electron energy under the action of an additional one-particle potential:

$$\tilde{v}(r) = \frac{1}{Z} \int_0^\infty d\mathbf{r}' \rho(r') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad (9)$$

where  $\rho(r)$  is the deformation of the distribution density in the core charge due to core polarization induced by a vacancy potential in the state  $n'l'$

$$\tilde{\tilde{v}} = \frac{1}{Z} \int d\mathbf{r}' |\phi_{n'l'}(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (10)$$

To find  $\rho(r)$  we used a Thomas–Fermi equation for the core electron density, taking into account  $\tilde{v}(r)$  and regarding it as a perturbation. The Thomas–Fermi method is known to give very good results for the electron density of the ion. After linearization, the Thomas–Fermi equation gives the following system of ordinary differential equations for the determination of the potential  $\tilde{v}(r)$ :

$$\begin{aligned} y'_1 &= R_{n'l}^2 r^2 \\ y'_2 &= -R_{n'l}^2(r)r \\ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \tilde{v} \right) &= -\frac{2}{\pi Z} [v(R_c) - v(r)]^{1/2} [\tilde{\tilde{v}}(R_c) - \tilde{\tilde{v}}(r) - \tilde{v}(r)] \end{aligned} \quad (11)$$

where

$$\tilde{\tilde{v}} = (y_1/r + y_2)/Z$$



and  $R_c$  is a conventional core radius. The system (11) has been solved numerically at the following boundary conditions:

$$y_1(0) = 0, \quad y_2(\infty) = 0, \quad \tilde{v}'(0) = 0, \quad \tilde{v}(R_c) = 0.$$

Equations for radial functions and for all necessary integrals over them have also been included in this system. Thus, the whole calculation has reduced to the solution of a system of ordinary differential equations.

## 5. Numerical results

For the states  $1s^22s^22p^53s^23p$  a calculation has been performed with a one-parameter potential  $v(r)$ , the parameter  $b$  in (4) having been determined from the ionization energy of the  $3p$  electron in the state  $1s^22s^22p^63s^23p$ ; with a two-parameter potential, parameters  $b$  and  $c_1$  have been determined by the ionization energy of electrons  $3p$  and  $2p$  (vacancy formation); and with a one-parameter potential but introducing different parameters  $b$  for the states of the vacancy  $2p$  and the outer electron  $3p$ . In all the three variants the zero energy is the same, the discrepancy in the form of  $v(r)$  influencing only the values of the radial integrals, which determine the effective vacancy–outer-electron energy interaction. The corrections which are due to the introduction of the second parameter  $c_1$  turned out to be small in the sense determined above; the third variant gives practically the same results as the second one (with accuracy up to  $10^{-5}$  cu). Therefore, in all cases we used the simplest potentials

$$v_{nl}(r) = -\{Z - N[1 - \exp(-b_{nl}r)]\}/Zr \quad (12)$$

and determined  $b_{nl}$  individually for electron and vacancy orbitals.

In table 1 radial integrals  $R_0(nl, n_1l_1; n_1l_1, nl)$  are given for the states with one valence electron  $nl$  and vacancy  $n_1l_1$  with and without account being taken of the higher-order corrections. These integrals determine the main part of the electron–vacancy interaction. It is seen from table 1 that the correction for the core polarization constitutes the main part of the higher-order correction for the case of the filling shell  $n = 3$  and decreases sharply for  $4s$  electrons. At the same time, a relative

**Table 1.** Radial integrals  $R_0(nl, n_1l_1; n_1l_1, nl)$  for the states with one electron  $nl$  in the outer shell: (a) first-order perturbation theory, (b) with account of core polarization, (c) with account of core polarization and core-field anti-shielding by a vacancy ( $Z = 26$ ).

	(a)	(b)	(c)
$R_0(1s3s; 3s1s)$	0.002930	0.002461	0.002516
$R_0(2s3s; 3s2s)$	0.002547	0.002169	0.002212
$R_0(2p3s; 3s2p)$	0.002599	0.002204	0.002212
$R_0(1s3p; 3p1s)$	0.002982	0.002508	0.002685
$R_0(2s3p; 3p2s)$	0.002568	0.002189	0.002319
$R_0(2p3p; 3p2p)$	0.002638	0.002241	0.002376
$R_0(1s3d; 3d1s)$	0.002495	0.002098	0.002218
$R_0(2s3d; 3d2s)$	0.002426	0.002092	0.002211
$R_0(2p3d; 3d2p)$	0.002444	0.002104	0.002225
$R_0(1s4s; 4s1s)$	0.000713	0.000695	0.000800
$R_0(2s4s; 4s2s)$	0.000693	0.000680	0.000780
$R_0(2p4s; 4s2p)$	0.000696	0.000682	0.000783

contribution of the core-field shielding by the vacancy increases with the filling of shells. These corrections have opposite signs. In table 2 integrals  $R_0(nl, n_1l_1; n_1l_1, nl)$  illustrate the influence of the filling shell on the effective interaction energy of one outer electron  $nl$  with the vacancy  $n_1l_1$ . These integrals are weighted in the full energy of the state with coefficient  $k$  equal to the number of electrons  $nl$  in the outer shell. Since the outer shell becomes more diffuse, this integral decreases with increase of  $k$ , the jump being especially great after the addition of one electron above the half-filled shell. These integrals should be linear over  $k$  up to second order, and the observed deviation from linearity is attributed to the effective account for the higher corrections and agrees with qualitative notions about the change in the diffuseness of the shell accompanying its filling.

**Table 2.** Radial integrals compared with the number of electrons ( $k$ ) in the outer shell of Fe ions.

$k$	$R_0(1s3p; 3p1s)$	$R_0(2s3p; 3p2s)$	$R_0(2p3p; 3p2p)$	$R_0(1s3d; 3d1s)$	$R_0(2s3d; 3d2s)$	$R_0(2p3d; 3d2p)$
1	0.002685	0.002319	0.002376	0.002218	0.002211	0.002225
2	0.002639	0.002290	0.002344	0.002161	0.002158	0.002170
3	0.002601	0.002266	0.002317	0.002081	0.002083	0.002094
4	0.002480	0.002178	0.002225	0.002001	0.002008	0.002017
5	0.002425	0.002153	0.002198	0.001965	0.001972	0.001982
6	0.002411	0.002132	0.002175	0.001757	0.001775	0.001782

In table 3 the results of the calculation of state energies with vacancies  $1s, 2s, 2p$  are summarized. For the states with outer-shell configurations  $3d^k (k > 2)$  and  $4s^k$ , only average values of the energies of the configurations have been calculated. In the case of states with vacancies  $3s$  and  $3p$ , the neglect of contributions from a part of the second-order diagrams containing the parameter  $(R_v/R_a)^2$  is not justified. However, for these states a similar calculation has been performed, the results being given in table 4. The energy of states without vacancies are taken from the tables of Moore (1949) and from *Ionization Potentials and Ionization Limits*. Table 5 represents energies of vacancies in different cores. Data given in tables 3 and 4 are sufficient for calculating the energy of any one-electron transition  $\Phi_i \rightarrow \Phi_f$ , where  $\Phi_i, \Phi_f$  are the states obtained from the state of the main configuration by removing any electron (outer or inner). In table 6 our results for some transition energies  $\Delta E$  averaged over configurations are compared with those of a Hartree-Fock calculation  $\Delta E_{\text{HF}}$  and with the compilation results  $\Delta E_A$  given by House (1969). The latter have been obtained by adding, for all Hartree-Fock wavelengths of House, a constant empirical correction that is found by comparison of calculated data with experimental literature or with extrapolated wavelengths for one of the known transitions in the Fe ion. The value  $\Delta E_0$  designates transition energies disregarding vacancy-outer-shell interactions. It may be seen from this table that the discrepancy of our results with those of Hartree-Fock exceeds the correction from the vacancy-outer-shell interaction calculated here. The transition to the  $\Delta E_A$  halves this discrepancy.

It should be noted, in conclusion, that the proposed calculation method allows a generalization to be made with the purpose of accounting for relativistic effects using the Dirac equation with a model potential of zeroth approximation in the form (3). At present we are calculating the real and imaginary parts of the relativistic energies of the states with vacancies. The imaginary part may be interpreted as the inverse lifetime of the states that may autoionize (Ivanov 1975).

**Table 3.** Energies of Fe ion states†.

$\Phi$	$nl$	$\Phi$	$-E$	$\Phi$	$nl$	$\Phi$	$-E$	$\Phi$	$nl$	$\Phi$	$-E$
$3s^2 3S$	—	$2S$	1-725016	$3p^3 2D$	—	$2D$	1-808375	$3d^2 1D$	—	$1D$	1-866293
	$1s$	$1S$	1-307066		$1s$	$1D$	1-400575		$1s$	$2D$	1-469513
	$1s$	$3S$	1-307335		$1s$	$3D$	1-400740		$2s$	$2D$	1-811586
	$2s$	$1S$	1-650979		$2s$	$1D$	1-743413		$2p$	$2P$	1-820732
	$2s$	$3S$	1-651432		$2s$	$3D$	1-743530		$2p$	$2D$	1-820810
	$2p$	$1P$	1-660236		$2p$	$1P$	1-752764		$2p$	$2F$	1-820832
	$2p$	$3P$	1-660412		$2p$	$3P$	1-752443	$3d^2 1S$	—	$1S$	1-866007
	—	$1S$	1-749847		$2p$	$1D$	1-752052		$1s$	$2S$	1-469227
	$1s$	$2S$	1-334491		$2p$	$3D$	1-752793		$2s$	$2S$	1-811300
	$2s$	$2S$	1-678263		$2p$	$1F$	1-752691		$2p$	$2P$	1-820519
$3s^2 1S$	$2p$	$2P$	1-687328		$2p$	$3F$	1-752749	$3d^2 3P$	—	$3P$	1-866263
	—	$2P$	1-771116	$3p^4 1S$	—	$1S$	1-823919		$1s$	$2P$	1-469481
	$1s$	$1P$	1-358321		$1s$	$2S$	1-418333		$1s$	$4P$	1-469485
	$1s$	$3P$	1-358495		$2s$	$2S$	1-760943		$2s$	$2P$	1-811390
	$2s$	$1P$	1-701778		$2p$	$2P$	1-769822		$2s$	$4P$	1-811639
	$2s$	$3P$	1-701901						$2p$	$2S$	1-820637
	$2p$	$1S$	1-709770	$3p^4 1D$	—	$1D$	1-824206		$2p$	$4S$	1-820637
	$2p$	$3S$	1-711267		$2D$	$2D$	1-418620		$2p$	$2P$	1-820496
	$2p$	$1P$	1-710901		$2D$	$2D$	1-761230		$2p$	$4P$	1-820966
	$2p$	$3P$	1-710701		$2P$	$2P$	1-770241		$2p$	$2D$	1-820675
$3p^2 1S$	$2p$	$1D$	1-710922		$2D$	$2D$	1-770370	$3d^2 1G$	—	$4D$	1-820834
	$2p$	$3D$	1-711047		$2P$	$2F$	1-740462		$2p$	$1G$	1-866209
	—	$1S$	1-790240	$3p^4 3P$	—	$3P$	1-824372		$1s$	$2G$	1-469429
	$1s$	$2S$	1-380079		$2P$	$2P$	1-418636		$2s$	$2G$	1-811502
	$2s$	$2S$	1-723176		$4P$	$4P$	1-418861		$2p$	$2F$	1-820694
	$2p$	$2P$	1-732297		$2P$	$2P$	1-761292		$2p$	$2G$	1-820622
	—	$1D$	1-790469		$4P$	$4P$	1-761449	$3d^2 3F$	—	$2H$	1-820818
	$1s$	$2D$	1-380308		$2S$	$2S$	1-770833		—	$3F$	1-866392
	$2s$	$2D$	1-723405		$2p$	$2S$	1-770341		$1s$	$2F$	1-469610
					$2p$	$4S$			$1s$	$4F$	1-469614

$3p^2\ ^1D$	2p	$^2P$	1-732411	$3p^4\ ^3P$	2p	$^2P$	1-770197	$3d^2\ ^3F$	2s	$^2F$	1-811519
	2p	$^2D$	1-732456		2p	$^4P$	1-770644		2s	$^4F$	1-811768
	2p	$^2F$	1-732625		2p	$^2D$	1-770353		2p	$^2D$	1-820515
	—				2p	$^4D$	1-770720		2p	$^4D$	1-821023
$3p^2\ ^3P$	—	$^3P$	1-790692						2p	$^2F$	1-820717
	1s	2p	1-380363	$3p^5\ ^2P$		$^2P$	1-836820		2p	$^4F$	1-820938
	1s	4p	1-380615		1s	$^1P$	1-435190		2p	$^2G$	1-820884
	2s	2p	1-723509		1s	$^3P$	1-435333		2p	$^4G$	1-821001
	2s	4p	1-723688		2s	$^1P$	1-777599	$3d^3$	—	—	1-871777
	2p	$^2S$	1-732623		2s	$^3P$	1-777701		1s	—	1-476919
	2p	4s	1-732623		2p	$^1S$	1-786306		2s	—	1-819085
	2p	2p	1-732200		2p	$^3S$	1-786879		2p	—	1-828312
	2p	4p	1-732979		2p	$^1P$	1-787064	$3d^4$	—	—	1-875858
	2p	$^2D$	1-732701		2p	$^3P$	1-786751		1s	—	1-482762
	2p	$^4D$	1-732837		2p	$^1D$	1-786573		2s	—	1-824949
$3p^3\ ^4S$	—	4s	1-808675		2p	$^3D$	1-786990		2p	—	1-834180
	1s	3s	1-400793					$3d^5$	—	—	1-878842
	1s	5s	1-401122	$3p^6\ ^1S$	—	$^1S$	1-851398		1s	—	1-487569
	2s	3s	1-743655		1s	$^2S$	1-450298		2s	—	1-829765
	2s	5s	1-743888		2s	$^2S$	1-792458		2p	—	1-839005
	2p	3p	1-752688		2p	$^2P$	1-801651	$3d^6$	—	—	1-880508
	2p	5p	1-753108						1s	—	1-489949
$3p^3\ ^2P$	—	2p	1-808185	$3d\ ^2D$	—	$^2D$	1-859603		2s	—	1-832221
	1s	1p	1-400385		1s	$^1D$	1-460718		2p	—	1-841452
	1s	3p	1-400550		1s	$^3D$	1-460721	$3d^6 4s$	—	—	1-881388
	2s	1p	1-743223		2s	$^1D$	1-802699		1s	—	1-491629
	2s	3p	1-743340		2s	$^3D$	1-802874		2s	—	1-833882
	2p	1s	1-751649		2p	$^1P$	1-811565		2p	—	1-843115
	2p	3s	1-752618		2p	$^3P$	1-812195	$3d^6 4s^2$	—	—	1-881816
	2p	1p	1-752545		2p	$^1D$	1-811966		1s	—	1-492795
	2p	3p	1-752375		2p	$^3D$	1-811966		2s	—	1-835033
	2p	1D	1-752288		2p	$^1F$	1-812014		2s	—	1-844268
	2p	3D	1-752574		2p	$^3F$	1-812113		2p	—	

†  $\Phi$  denotes the state of the open shell,  $nl$  the state of the vacancy and  $\Phi$  denotes the term of the whole state.

**Table 4.** Energies of states for Fe ions with the vacancy 3s or 3p.†

$\Phi$	$nl$	$\Phi$	$-E$	$\Phi$	$nl$	$\Phi$	$-E$
$3p^2\ ^2P$	3s	$^1P$	1.747353	$3d^2\ ^1S$	3s	$^2S$	1.854197
	3s	$^3P$	1.748240		3p	$^2P$	1.856563
$3p^2\ ^1S$	3s	$^2S$	1.768752	$3d^2\ ^3P$	3s	$^2P$	1.854199
$3p^2\ ^1D$	3s	$^2D$	1.768981		3s	$^4P$	1.854685
	3s	$^2P$	1.768325		3p	$^2S$	1.856662
$3p^2\ ^3P$	3s	$^4P$	1.769643		3p	$^4S$	1.856662
	3s	$^3S$	1.787739		3p	$^2P$	1.856055
$3p^3\ ^4S$	3s	$^5S$	1.789484	$3d^2\ ^1G$	3p	$^4P$	1.856661
	3s	$^1P$	1.787685		3p	$^2D$	1.856583
$3p^3\ ^2P$	3s	$^3P$	1.788558		3p	$^4D$	1.856986
	3s	$^1D$	1.787875		3s	$^2G$	1.854399
$3p^3\ ^2D$	3s	$^3D$	1.788747		3p	$^2F$	1.856611
	3s	$^2S$	1.805592	$3d^2\ ^3F$	3p	$^2G$	1.856665
$3p^4\ ^1S$	3s	$^2D$	1.805879		3p	$^2H$	1.856946
	3s	$^2P$	1.805188		3s	$^2F$	1.854258
$3p^4\ ^3P$	3s	$^4P$	1.806474		3s	$^4F$	1.854744
	3s	$^1P$	1.821231		3p	$^2D$	1.855987
$3p^5\ ^2P$	3s	$^3P$	1.822081		3p	$^4D$	1.857212
	3s	$^2S$	1.836210	$3d^3$	3p	$^2F$	1.856530
$3d^2\ ^2D$	3s	$^1D$	1.845883		3p	$^4F$	1.857073
	3s	$^3D$	1.846214	$3d^4$	3p	$^2G$	1.856866
	3p	$^1P$	1.847340		3p	$^4G$	1.857176
	3p	$^3P$	1.848802	$3d^5$	3s	—	1.861775
	3p	$^1D$	1.848437		3p	—	1.864190
	3p	$^3D$	1.848437	$3d^6$	3s	—	1.867408
	3p	$^1F$	1.848419		3p	—	1.869839
	3p	$^3F$	1.848672	$3d^6\ 4s$	3s	—	1.871946
$3d^2\ ^1D$	3s	$^2D$	1.854483		3p	—	1.874391
	3p	$^2P$	1.856714		3s	—	1.874671
	3p	$^2D$	1.856827		3p	—	1.877042
	3p	$^2F$	1.856924		3s	—	1.876301
				$3d^6\ 4s^2$	3p	—	1.878670
					3p	—	1.877429
							1.879796

† See notes to table 3.

**Table 5.** The energy of one vacancy in the core.

Vacancy	$1s^22s^22p^6$	$1s^22s^22p^63s^2$	$1s^22s^22p^63s^23p^6$	$1s^22s^22p^63s^23d^6$
1s	0.420197†	0.415356	0.401100	0.390559
2s	0.075796†	0.071584	0.058940	0.048287
2p	0.066816†	0.062519	0.049747	0.039056
3s	—	0.024831‡	0.015188‡	0.005837
3p	—	—	0.012778	0.003466

† Calculated from the data of Knight (1969) and Ivanova and Safronova (1975).

‡ Taken from Moore (1949) and *Ionization Potentials and Ionization Limits*.

Other values have been obtained by adding vacancy-filled subshells interaction energy.

**Table 6.** Transition energies 1s–2p averaged over the terms.

Transition	$\Delta E$	$\Delta E_0$	$\Delta E_{\text{HF}}$	$\Delta E_{\text{A}}$
1s2s <sup>2</sup> 2p <sup>6</sup> –1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	0.3534	0.3534	0.3468	0.3499
1s2s <sup>2</sup> 3s–1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup> 3s	0.3531	0.3534	0.3466	0.3497
1s2s <sup>2</sup> 3s <sup>2</sup> –1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup> 3s <sup>2</sup>	0.3528	0.3534	0.3463	0.3493
1s2s <sup>2</sup> 3s <sup>2</sup> 3p–1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup> 3s <sup>2</sup> 3p	0.3525	0.3528	0.3461	0.3491

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