Ab initio fully relativistic calculations of x-ray spectra of highly charged ions

S. Kotochigova,[1] K. P. Kirby,[2] and I. Tupitsyn[3]
[1]*Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA*
[2]*Institute for Theoretical Atomic, Molecular and Optical Physics, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, USA*
[3]*St. Petersburg State University, St. Petersburg, Russia*
(Received 1 October 2007; published 21 November 2007)

We have developed and applied an *ab initio* fully relativistic method for precise calculations of outer-shell transitions in highly charged ions. This method is based on the multiconfiguration Dirac-Fock-Sturm theory in combination with Brillouin-Wigner many-body perturbation theory. We demonstrate the capability of the method through calculations of the $3s$, $3d \rightarrow 2p$ transitions in Fe XIX. The basis set, constructed out of Dirac-Fock and Sturm one-electron wave functions, allows calculations with an accuracy of less than a few 10^{-3} Å for the wavelengths and better than 1% for the oscillator strengths. Some of the transitions given here have not been observed or calculated previously.

DOI: 10.1103/PhysRevA.76.052513 PACS number(s): 31.10.+z, 31.15.Ar, 32.30.Rj

I. INTRODUCTION

The current project is intended to establish "benchmark" atomic data that can be used for plasma diagnostics, primarily for x-ray astrophysics. We introduce an *ab initio* computational method to calculate properties of highly charged few-electron ions and provide accurate and complete atomic data on the electronic structure and L-shell oscillator strengths of the Fe XIX ion. Detailed understanding of these ions are needed for modeling of x-ray spectra observed in laboratories and satellite-borne telescopes. Iron ions play a critical role in the determination of the ionization and temperature structure in astrophysical x-ray sources.

A calculation of highly charged few-electron ions requires full implementation of relativistic, correlation, and quantum electrodynamics effects. In this work, the Dirac-Fock method is used to solve both the Dirac-Coulomb-Breit and Dirac-Coulomb-Sturm equations to generate spatially localized single-electron basis functions from which configuration state functions (CSFs) are constructed. The CSFs are linear combinations of the Slater determinants. Large scale configuration interaction (CI) is used to include the major correlation effects. In addition, many-body Brillouin-Wigner perturbation theory adds high-order correlation. We include the frequency-dependent Breit interaction, quantum electrodynamics corrections (QED), nuclear size effects, and other high-order relativistic contributions beyond the Dirac theory in the many-body Hamiltonian. Calculation of transition dipole moments is carried out with nonorthogonal single-electron orbitals, as orbitals are separately optimized for the initial and final state. We use a relativistic atomic physics software suite developed in this and earlier studies [1–4].

The study of L-shell emission lines of iron has been a subject of considerable interest over the past two decades. Early semiempirical studies by Fawcett [5] and Bhatia *et al.* [6] provided accurate wavelengths and oscillator strengths of L-shell $2p$-$3s$ and $2p$-$3d$ transitions in Fe XIX. The most intense lines of solar flare spectra were used as input for the semiempirical analyses.

A large scale compilation of spectral data for Fe XIX as well as other iron ions has been performed by Shirai *et al.* [7] and published at the National Institute of Standards and Technology, Reference Data Center website [8]. It contains critically evaluated energy levels, wavelengths and transition probabilities for a large number of atoms and ions, including data on $2p^4-2p^3 3s$, $3d$ transitions in Fe XIX. The compilation is based on the original literature.

New opportunities for the observation of a large number of x-ray transitions of iron ions arose with the launch of two high-resolution satellite-based observatories, Chandra and XMM-Newton. Their observations now provide a wealth of spectra showing L-shell emission lines of iron. Quantitative analyses of these spectra require a higher level of accuracy and completeness of the atomic data than has been available previously. In addition, detailed studies of Fe XVIII–XXIV x-ray emission lines have been performed at the Lawrence Livermore National Laboratory using the electron beam ion trap EBIT-II [9]. The results of the latter measurements have been identified by employing predictions of the Hebrew University-Lawrence Livermore Atomic Code (HULLAC) [10]. HULLAC is based on a multiconfiguration relativistic parametric-potential method and can calculate atomic energies and transition probabilities. While the identification of bright lines is satisfactory, weak lines, line blending, and an incomplete list of the spectral lines add uncertainty to the interpretation.

A more sophisticated method of calculating L-shell ions of iron has been used by Gu [11]. A combination of configuration interaction and many-body perturbation theory allowed the author to reduce the uncertainty in the wavelengths, obtained by HULLAC [9], from 40–60 mÅ to 10 mÅ for most of the calculated lines.

In this paper we present another way to obtain energy levels of highly charged iron ions. The major difference between our calculation and that of Ref. [11] is the use of localized single-electron Sturmian functions to describe unoccupied excited orbitals. This allows us to construct much larger CI matrices to better account for correlation. In addition, we use many-body Brillouin-Wigner perturbation theory rather than Schrödinger perturbation theory used by [11]. In Sec. III we compare our results with data obtained by experimental and other theoretical studies.

II. THEORY

We use an *ab initio* multiconfiguration Dirac-Fock-Sturm method (MDFS) combined with a second-order Brillouin-Wigner many-body perturbation theory (BW-MBPT) for a precise evaluation of transition wavelengths and oscillator strengths of iron ions emitting in the x-ray region. The many-electron wave functions of the initial and final states are expanded in terms of orthogonal configuration state functions (CSFs). Sets of CSFs are generated by including all single and double excitations with additional triple excitations of valence orbitals from a "reference" CSF. Orbitals used to construct each CSF in the calculation of the initial and final state have been separately optimized, and thus are nonorthogonal. Therefore the evaluation of the oscillator strengths has to be done accounting for this nonorthogonality. We have included the finite size of the Fe nucleus that has a nonzero effect on the orbitals of s and p type. The potential energy due to the finite nuclear size is defined by the charge density of the nucleus [12] that can be expressed in the case of a uniformly charged sphere in terms of the atomic mass number, A, which for iron is equal to 55.845 a.m.u.

A. Configuration state functions

In our approach configuration state functions are constructed as linear combinations of antisymmetrized products of N valence or virtual one-electron orbitals. Valence orbitals are orbitals that are occupied in the reference CSF of either the initial or final state of the ion, while virtual orbitals are those that are not occupied in these reference CSFs. In our relativistic calculation a one-electron orbital is a four-component Dirac spinor (throughout this paper we will use atomic units)

$$\psi_{nkm}(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} P_{nk}(r) & \chi_{km}(\theta,\phi) \\ iQ_{nk}(r) & \chi_{-km}(\theta,\phi) \end{pmatrix}, \tag{1}$$

that is labeled by a principal quantum number n, k, and projection m. The latter two labels are eigenvalues of the spin-orbital operator $-(1+\vec{\sigma}\cdot\vec{L})$, where $\vec{\sigma}$ are the three Pauli matrices and $\vec{L}$ is the single-electron orbital angular momentum operator around the nucleus of the ion. For eigenvalues k, m the spin-orbital eigenfunction is $\chi_{km}(\theta,\phi)$. Note that k uniquely determines the orbital angular momentum l, the eigenvalue of the operator $\vec{L}$, and the total electron angular momentum j via $k=l(l+1)-(j+1/2)^2$ and $j=l+1/2$ or $l-1/2$. The quantity m is the projection of j along a space fixed axis. Finally, $P_{nk}(r)$ and $Q_{nk}(r)$ are the large and small components of the Dirac spinor, respectively. The spherical coordinates r, θ, and ϕ are used to specify the position of the electron with respect to the nucleus of the atom.

Valence orbitals as defined in Eq. (1) are obtained by solving the coupled nonlocal Dirac-Fock (DF) equations simultaneously and self-consistently [13]. In terms of major and minor components we have for the shell nk

$$c\left(-\frac{d}{dr}+\frac{k}{r}\right)P_{nk}+[-2c^2+V_c]Q_{nk}+U^Q_{nk} = \varepsilon_{nk}Q_{nk}+\sum_{n\neq n'}\frac{\lambda_{nk,n'k}}{q_{nk}}Q_{n'k}, \tag{2}$$

and

$$c\left(-\frac{d}{dr}+\frac{k}{r}\right)Q_{nk}+V_cP_{nk}+U^P_{nk} = \varepsilon_{nk}P_{nk}+\sum_{n\neq n'}\frac{\lambda_{nk,n'k}}{q_{nk}}P_{n'k}, \tag{3}$$

where c is the speed of light, V_c is the total DF Coulomb potential, U^P_{nk} and U^Q_{nk} are nonlocal exchange potentials that depend on all orbitals with $n'k'\neq nk$, $\lambda_{nk,n'k}$ are off-diagonal Lagrange multipliers which arise from the orthonormality constraints on the orbitals, and q_{nk} are the occupation numbers of the shell nk.

Our calculations show that the radius of the Dirac-Fock orbitals grows rapidly with the level of excitation, i.e., the principle quantum number n. Consequently, the spatial overlap between orbitals becomes progressively smaller, and the use of highly excited orbitals in a configuration interaction or perturbation theory expansion is not optimal as the convergence of the eigenvalues with increasing numbers of orbitals is slow. An alternative to the Dirac-Fock orbitals is the use of Sturm functions [14–17] to describe excited unoccupied virtual orbitals. These orbitals are used to increase the flexibility of the atomic wave function. Compact Sturm orbitals are obtained by solving the Sturm-Dirac (SD) equations

$$c\left(-\frac{d}{dr}+\frac{k}{r}\right)\hat{P}_{nk}+[-2c^2+V_c-\varepsilon_{n_0k}]\hat{Q}_{nk}+U^Q_{nk} = \mu_{nk}W_k\hat{Q}_{nk}+\sum_{n\neq n'}\frac{\lambda_{nk,n'k}}{q_{n_0k}}Q_{n'k} \tag{4}$$

and

$$c\left(-\frac{d}{dr}+\frac{k}{r}\right)\hat{Q}_{nk}+[V_c-\varepsilon_{n_0k}]\hat{P}_{nk}+U^P_{nk} = \mu_{nk}W_k\hat{P}_{nk}+\sum_{n\neq n'}\frac{\lambda_{nk,n'k}}{q_{n_0k}}P_{n'k}, \tag{5}$$

where the energies $\varepsilon_{n0,k}$ are set equal to the Dirac-Fock energies of the n,k orbitals. In this case $\lambda_{nk,n'k}=0$ is an eigenvalue of the Sturm-Dirac equations and the corresponding Sturm functions are equal to the corresponding DF orbitals. For the eigenvalues $\lambda_{nk,n'k}>0$ we label the Sturm functions according to the values k and μ of the DF orbital and $n'>n$ increasing for increasing $\lambda_{nk,n'k}$. The weight function W_k is given by

$$W_k(r) = -\frac{1-\exp[-(\zeta_k r)^2]}{(\zeta_k r)^2}. \tag{6}$$

For $\zeta_k r \ll 1$ the weight function approaches unity while for

$\zeta_k r \gg 1$ it approaches zero as $1/r^2$, faster than a Coulomb potential. The parameters ζ_k are chosen to ensure that the $W_k(r)$ are approximately constant in the vicinity of the atomic core and do not distort the DF orbitals.

To construct the antisymmetric N-electron atomic wave functions of an iron ion from one-electron wave functions $\psi_i(\vec{r})$ of Eq. (1) we use Slater determinants $\det[\psi_1(\vec{r}_1),\ldots,\psi_N(\vec{r}_N)]/\sqrt{N!}$

In order to obtain CSFs from Slater determinants additional conditions have to be satisfied. The first condition is associated with the spherical symmetry of the problem: This requires that a CSF must be an eigenfunction of operators $\hat{J}^2$ and $\hat{J}_Z$ (the square of the total angular momentum and its projection on the Z axis). The determinants are eigenfunctions of $\hat{J}_Z$ but, in general, they are not eigenfunctions of the operator $\hat{J}^2$. These eigenfunctions are constructed as a linear combination

$$\Phi(CSF,JM) = \sum C(JM|j_1 m_1,\ldots)\det[\psi_1(\vec{r}_1),\ldots,\psi_N(\vec{r}_N)], \tag{7}$$

where sum is over $m_1,\ldots,m_N$ such that $m_1+\cdots+m_N=M$ with a suitably chosen set of parameters $C(JM|j_1 m_1,\ldots)$. The parameters $C(JM|j_1 m_1,\ldots)$ are found for each relativistic configuration by diagonalization of matrix $\hat{J}^2$ with the condition $\Sigma|C(JM|j_1 m_1,\ldots)|^2=1$ and the orthogonality of the one-electron orbitals $(\psi_i,\psi_j)=\delta_{ij}$. In addition, the CSF has to be constructed from the many-electron wave function which belongs to the configuration $(n_1 l_1 j_1)^{q_1}\ldots(n_A l_A j_A)^{q_A}$ so that we select determinants in which q_1 one-electron functions belong to shell $n_1 l_1 j_1$, and so on. Notice that for convenience we use the notation $n\ell j$ instead of $n\kappa$ to label the orbital $\psi_{n\kappa\mu}$. Both notations uniquely define a relativistic orbital. Note also that every nonrelativistic configuration can be split into several relativistic configurations. Finally, we ensure that all CSFs are orthonormal.

B. Configuration interaction approach with QED effects

Fe XIX has open shells in both the initial and final states of the x-ray transitions considered here. For quantitative agreement between experiment and theory a configuration interaction approach is needed. This section describes our implementation where we allow CSFs in both the initial and final states to be nonorthogonal.

The total wave function of either the initial or final state is given by a linear combination of CSF wave functions (7)

$$\Psi(\mathbf{r}) = \sum_\alpha c_\alpha \Phi_\alpha(JM), \tag{8}$$

where α labels CSFs. The configuration interaction (CI) coefficients c_α are obtained by solving the eigenvalue matrix problem

$$\sum_{\alpha'} \mathbf{H}_{\alpha\alpha'}\mathbf{c}_{\alpha'} = E\mathbf{c}_\alpha, \quad \mathbf{H}_{\alpha\alpha'} = \langle\alpha|\hat{H}_D|\alpha'\rangle, \tag{9}$$

where $\hat{H}_D$ is the total atomic Hamiltonian operator

TABLE I. List of relativistic and QED contributions used in the calculation.

Self-energy	Relativistic recoil
Vacuum polarization	Two-photon corrections
Finite nuclear size	Nuclear size correction
Nuclear polarization	Nuclear self-energy
Radiative-recoil correction to self-energy and vacuum polarization	

$$\hat{H}_D = \sum_i \hat{h}_i + \sum_{i>j} \hat{V}_{ij}, \tag{10}$$

and $\hat{h}_i = c\vec{\alpha}_i\cdot\vec{p}_i + \beta_i c^2 - Z/r_i$ is the Dirac operator for electron i in the field of a nucleus of charge Z. Here $\vec{\alpha}$ and $\hat{\beta}$ are the Dirac matrices and $\vec{p}$ is the momentum of the electron. The potentials $\hat{V}_{ij} = 1/|r_i - r_j| + V_B$ are the sum of the electron-electron Coulomb and Breit interaction. The Breit interaction consists of two terms, the magnetic and retardation interactions [13].

To construct the matrix elements $\mathbf{H}_{\alpha\alpha'}$ we use an approach that combines configuration interaction with second-order Brillouin-Wigner perturbation theory. The total configuration space in our method is divided into two parts based on the idea that an eigenfunction $\Psi(\mathbf{r})$ has one dominant major configuration. The principal configuration space ($\mathcal{P}$) includes the major configurations that are important for the electric dipole transitions and those that have strong correlation with the major configurations. Configurations that include highly excited virtual orbitals with marginal contributions in the correlation interaction form a complementary part of the configuration space ($\mathcal{Q}$) [18]. In our approach coupling between CSFs in the $\mathcal{P}$ space and between states in the $\mathcal{P}$ and $\mathcal{Q}$ space is implemented in the Hamiltonian. In the $\mathcal{Q}$ space only the diagonal terms are included

$$\langle\alpha|H^{\mathcal{QQ}}|\alpha'\rangle = H^{\mathcal{QQ}}_{\alpha\alpha'} = E^{\mathcal{QQ}}_\alpha \delta_{\alpha,\alpha'}, \tag{11}$$

so that the Hamiltonian equation (9) can be written as

$$\sum_{\alpha'} \begin{pmatrix} H^{\mathcal{PP}}_{\alpha\alpha'} & H^{\mathcal{PQ}}_{\alpha\alpha'} \\ H^{\mathcal{PQ}}_{\alpha\alpha'} & H^{\mathcal{QQ}}_{\alpha\alpha'} \end{pmatrix} \mathbf{c}_{\alpha'} = E\mathbf{c}_\alpha. \tag{12}$$

The fact that the matrix $H^{\mathcal{QQ}}_{\alpha\alpha'}$ is diagonal significantly decreases the number of matrix elements that need to be stored and reduces the computational time of our iterative eigenvalue solver. It allows us to include a very large number of configurations which is practically impossible in a full CI.

We evaluated the high-order relativistic, quantum electrodynamic, and nuclear size corrections by calculating the one-electron Lamb shifts $\delta E^{n\ell}(Z)$ using an approach developed in [19] and applying an effective nuclear charge Z_{eff}. The list of the relevant theoretical contributions to $\delta E^{n\ell}(Z)$ is shown in Table I. Z_{eff} was found from the requirement that the

TABLE II. The total energies, Breit interaction, frequency-dependent Breit interaction, and QED corrections of the six ground-state levels of Fe XIX. Corrections are included in the total energies. All energies are given in atomic units.

State	J	Total energy	Breit	Freq. Breit	QED
$1s^22s^22p_{1/2}^22p_{3/2}^2$	2	−1051.848 573 692	0.386 022 38	−0.000 645 26	0.305 589 08
$1s^22s^22p_{1/2}^22p_{3/2}^2$	0	−1051.505 131 472	0.388 794 27	−0.000 742 72	0.305 890 97
$1s^22s^22p_{1/2}2p_{3/2}^3$	1	−1051.440 931 861	0.380 025 45	−0.000 892 51	0.306 615 82
$1s^22s^22p_{1/2}2p_{3/2}^3$	2	−1051.078 227 635	0.373 102 61	−0.000 868 25	0.306 515 15
$1s^22s^22p_{3/2}^4$	0	−1050.364 352 384	0.376 257 30	−0.001 050 81	0.306 749 18

one-electron charge density of each $n\ell$ atomic orbital is equal to the Dirac-Fock electron charge density of the same orbital at the Compton wavelength (R_c) distance from the nucleus:

$$\rho_{Z_{\text{eff}}}^{nl}(R_c) = \rho_{\text{DF}}^{nl}(R_c). \tag{13}$$

The QED corrections $\delta E^{n\ell}(Z_{\text{eff}})$ for the particular Z_{eff} and $n\ell$ are obtained by interpolations of the one-electron Lamb shifts $\delta E^{n\Sigma}(Z)$. The total QED correction for a particular CSF includes a sum of $\delta E^{n\ell}(Z_{\text{eff}})$ over all atomic orbitals that appear in the CSF.

C. Transition probabilities and oscillator strengths

We consider electric dipole transitions between the final state A and the initial state B with total angular momentum J_A and J_B, respectively. Since levels A and B are degenerate, the calculation of the total transition probability requires summation over the projections M_a of the final state and averaging over the projections M_b of the initial state. The Einstein $A^{(e)}$ coefficients for electric dipole transitions define the probability per unit time to emit a photon with an angular momentum K and frequency ω as

$$A_K^{(e)}(B \to A) = 2\tilde{\alpha}\omega \frac{2K+1}{2J_B+1} \sum_{M_b} \sum_{M_a} \sum_{Q} |\langle \alpha | \mathbf{T}_{KQ}^{(e)} | b \rangle|^2, \tag{14}$$

where $\tilde{\alpha}$ is the fine structure constant and a and b denote the final and initial state with projection M_a and M_b, respectively. The electric dipole transition operator $\mathbf{T}_{KQ}^{(e)}$ is a spherical tensor operator of rank K and projection Q and according to [20,21] is given in terms of scalar Y_{KQ} and vector $\vec{Y}_{KQ}^{K}$ spherical harmonics as

$$\mathbf{T}_{KQ}^{(e)} = -i\sqrt{\frac{4\pi}{2K+1}}[-V_{K+1}(r)\vec{\alpha}\cdot\vec{Y}_{KQ}^{K+1} + V_{K-1}(r)\vec{\alpha}\cdot\vec{Y}_{KQ}^{K-1} + iG_K V_K(r) Y_{KQ}], \tag{15}$$

where

$$V_{K+1}(r) = \sqrt{\frac{1}{2K+1}}[\sqrt{K} + G_K\sqrt{K+1}]j_{K+1}(\omega r/c),$$

$$V_K(r) = j_K(\omega r/c),$$

$$V_{K-1}(r) = \sqrt{\frac{1}{2K+1}}[\sqrt{K+1} - G_K\sqrt{K}]j_{K-1}(\omega r/c), \tag{16}$$

TABLE III. The total energies, Breit interaction, frequency-dependent Breit interaction, and QED corrections of the excited $1s^22s^22p^33s$ levels of Fe XIX. Corrections are included in the total energies. All energies are given in atomic units.

State	J	Total energy	Breit	Freq. Breit	QED
$1s^22s^22p_{1/2}2p_{3/2}^23s$	2	−1021.633 429 347	0.362 620 02	−0.000 478 89	0.309 982 88
$1s^22s^22p_{1/2}^22p_{3/2}3s$	1	−1021.403 413 885	0.364 907 91	−0.000 444 64	0.309 882 38
$1s^22s^22p_{1/2}2p_{3/2}^23s$	2	−1020.925 694 844	0.366 842 75	−0.000 479 00	0.309 975 48
$1s^22s^22p_{1/2}2p_{3/2}^23s$	1	−1020.915 125 591	0.366 297 44	−0.000 506 61	0.310 116 52
$1s^22s^22p_{1/2}2p_{3/2}^23s$	3	−1020.777 548 636	0.347 561 97	−0.000 832 79	0.310 521 21
$1s^22s^22p_{1/2}2p_{3/2}^23s$	2	−1020.688 734 796	0.349 901 99	−0.000 583 98	0.310 496 06
$1s^22s^22p_{1/2}2p_{3/2}^23s$	0	−1020.384 456 337	0.363 712 10	−0.000 598 95	0.310 126 96
$1s^22s^22p_{1/2}2p_{3/2}^23s$	1	−1020.350 633 245	0.362 167 38	−0.000 605 88	0.310 168 08
$1s^22s^22p_{3/2}^33s$	2	−1020.095 913 140	0.347 672 54	−0.000 832 79	0.311 151 14
$1s^22s^22p_{3/2}^33s$	1	−1020.025 604 003	0.348 892 74	−0.000 822 04	0.311 093 28

TABLE IV. X-ray wavelengths and oscillator strengths for all transitions from fine structure levels of the upper $1s^2 2s^2 2p^3 3s$, and $3d$ configurations to the lower $1s^2 2s^2 2p^4$ ground state configuration of Fe XIX. The first and second column are the total electron angular momentum of the upper and lower state, respectively. The next three columns give our results for the wavelengths and oscillator strengths in the velocity and length gauge. The transition wavelengths in columns labeled EBIT, HULLAC, NIST, Gu 2005, and Bhatia *et al.* are from Refs. [9,8,11,6], respectively. The column EBIT contains experimental data, where the number in parenthesis is the uncertainty.

Current MDFS data					EBIT	HULLAC	NIST	Gu 2005	Bhatia *et al.*
J	J'	λ(Å)	f_{velocity}	f_{length}	λ(Å)	λ(Å)	λ(Å)	λ(Å)	λ(Å)
				$1s^2 2s^2 2p^3 3s \rightarrow 1s^2 2s^2 2p^4$					
1	2	14.318	0.000 384	0.000 384					
2	2	14.349	0.003 602	0.003 604					14.349
1	2	14.466	0.001 662	0.001 665					
1	0	14.474	0.004 742	0.004 715					
1	1	14.504	0.000 735	0.000 733					
2	1	14.536	0.032 320	0.032 330			14.534		14.533
2	2	14.622	0.003 863	0.003 859					14.624
1	0	14.625	0.064 100	0.064 200				14.6288	14.625
1	1	14.655	0.005 608	0.005 612					14.657
3	2	14.660	0.046 730	0.046 770	14.664(7)	14.680	14.668	14.6669	14.662
0	1	14.671	0.011 210	0.011 220			14.668		14.673
1	2	14.673	0.017 970	0.017 940					14.673
2	2	14.706	0.019 450	0.019 450					14.703
1	2	14.729	0.000 092	0.000 091					
2	2	14.734	0.029 130	0.029 150	14.725(7)	14.757	14.735	14.7366	14.738
2	1	14.816	0.014 230	0.014 240			14.823	14.8193	14.816
1	2	14.828	0.009 564	0.009 568					
1	0	14.895	0.018 110	0.018 160					14.898
1	1	14.926	0.038 920	0.038 970	14.917(9)	14.943	14.929	14.9292	14.930
2	1	14.931	0.014 020	0.014 040		14.948	14.929	14.9336	14.933
1	2	14.966	0.044 970	0.044 980	14.980(5)	14.985	14.966	14.9680	14.977
2	2	14.993	0.069 310	0.069 390			14.995	14.9958	14.992
1	0	15.018	0.129 100	0.129 700			15.015		15.018
3	2	15.032	0.004 929	0.004 942				15.0396	15.032
2	2	15.080	0.003 678	0.003 687	15.079(4)	15.109)		15.0810	15.083
1	2	15.106	0.002 717	0.002 719					
2	2	15.111	0.003 513	0.003 516			15.111	15.1129	15.113
1	0	15.136	0.049 360	0.049 450	15.134(5)	15.151	15.138	15.1388	15.145
1	1	15.169	0.019 420	0.019 440	15.177(8)	15.182	15.172	15.1711	15.178
1	0	15.181	0.004 569	0.004 616					
2	1	15.286	0.000 187	0.000 188		15.308		15.2873	
1	2	15.354	0.000 465	0.000 467					
1	0	15.472	0.001 863	0.001 881					
2	2	15.474	0.000 015	0.000 015					
1	0	15.733	0.000 009	0.000 010					
				$1s^2 2s^2 2p^3 3d \rightarrow 1s^2 2s^2 2p^4$					
3	2	13.249	0.032 180	0.032 170				13.2513	13.255
1	2	13.279	0.000 901	0.000 902					
2	2	13.288	0.009 932	0.009 930					13.291
1	2	13.324	0.002 581	0.002 575					13.330
2	2	13.357	0.027 010	0.026 950					13.364
3	2	13.382	0.012 290	0.012 290					13.388

TABLE IV. (*Continued.*)

Current MDFS data					EBIT	HULLAC	NIST	Gu 2005	Bhatia *et al.*
J	J'	λ(Å)	f_{velocity}	f_{length}	λ(Å)	λ(Å)	λ(Å)	λ(Å)	λ(Å)
2	2	13.394	0.000 313	0.000 313					
1	0	13.413	0.104 300	0.104 100					13.414
3	2	13.424	0.161 200	0.161 100	13.423(4)	13.429	13.424	13.4264	13.427
1	1	13.438	0.371 700	0.371 400				13.4411	13.441
2	1	13.448	0.090 830	0.090 800				13.4502	13.449
1	0	13.459	1.298 000	1.297 000	13.462(3)	13.474			13.463
1	2	13.460	0.234 200	0.234 000		13.474		13.4634	13.469
0	1	13.467	0.130 300	0.130 200					13.468
2	2	13.480	0.019 430	0.019 440				13.4835	13.486
1	1	13.485	0.003 136	0.003 124					13.490
1	2	13.499	0.024 680	0.024 670					13.507
2	2	13.502	0.407 900	0.407 600	13.497(5)	13.515		13.5052	13.506
2	1	13.518	0.370 300	0.370 200				13.5229	13.524
3	2	13.518	0.698 000	0.697 600	13.518(2)	13.524	13.520	13.5235	13.519
1	2	13.538	0.041 090	0.041 050				13.5412	13.546
2	2	13.551	0.106 500	0.106 500	13.551(5)	13.570		13.5545	13.560
3	2	13.553	0.001 861	0.001 861					
2	1	13.557	0.043 050	0.043 040					
1	2	13.584	0.007 383	0.007 379					13.586
2	2	13.593	0.007 006	0.007 000					13.595
1	0	13.598	0.000 121	0.000 122					
1	2	13.623	0.020 120	0.020 090				13.6258	
1	1	13.624	0.013 440	0.013 440					13.631
1	2	13.631	0.010 870	0.010 870					13.636
3	2	13.633	0.019 260	0.019 260				13.6353	13.638
1	0	13.638	0.094 980	0.094 970					13.643
3	2	13.644	0.094 440	0.094 370	13.645(4)	13.658		13.6464	13.644
2	1	13.645	0.033 490	0.033 460					13.649
1	1	13.664	0.239 200	0.239 100		13.674		13.6687	13.669
2	2	13.665	0.031 130	0.031 100				13.6697	13.667
2	2	13.666	0.140 000	0.140 400		13.682		13.6672	13.671
2	1	13.668	0.069 620	0.069 490		13.675		13.6704	
0	1	13.673	0.064 810	0.064 790					13.679
1	0	13.677	0.133 900	0.133 700	13.676(4)	13.689		13.6808	13.683
3	2	13.692	0.072 910	0.072 930				13.6957	13.697
1	1	13.703	0.008 913	0.008 909					13.710
2	2	13.705	0.057 450	0.057 390		13.687			13.711
2	1	13.718	0.443 100	0.443 100			13.735	13.7209	13.725
3	2	13.736	0.342 000	0.341 700			13.735	13.7380	13.738
1	0	13.764	0.281 600	0.281 300		13.780		13.7672	13.770
1	2	13.774	0.075 030	0.074 980				13.7767	13.781
1	1	13.791	0.001 581	0.001 573					
3	2	13.794	0.236 800	0.236 500	13.795(5)	13.807	13.795	13.7955	13.793
1	2	13.795	0.004 218	0.004 219	13.759(5)	13.792			
2	2	13.795	0.147 700	0.147 700				13.7978	13.798
0	1	13.808	0.000 036	0.000 035					
1	2	13.814	0.011 090	0.011 110					13.821

TABLE IV. (*Continued.*)

Current MDFS data					EBIT	HULLAC	NIST	Gu 2005	Bhatia *et al.*
J	J'	λ(Å)	f_{velocity}	f_{length}	λ(Å)	λ(Å)	λ(Å)	λ(Å)	λ(Å)
2	2	13.818	0.000 007	0.000 008					
2	1	13.834	0.019 140	0.019 100				13.8365	13.834
3	2	13.834	0.014 360	0.014 380			13.837	13.8372	13.833
2	2	13.845	0.053 150	0.053 150		13.859		13.8465	13.844
1	2	13.855	0.038 500	0.038 510	13.839(5)	13.875		13.8582	13.861
2	2	13.869	0.008 015	0.008 007					13.876
1	0	13.879	0.074 330	0.074 380					13.881
1	0	13.928	0.002 231	0.002 282					13.938
1	2	13.931	0.004 809	0.004 795				13.9312	13.932
2	2	13.933	0.007 413	0.007 399	13.934(8)	13.954		13.9329	13.932
3	2	13.934	0.001 839	0.001 854		13.954		13.9345	13.935
1	0	13.940	0.339 700	0.339 300		13.952		13.9434	
1	2	13.944	0.022 840	0.022 810		13.954		13.9468	13.951
3	2	13.954	0.011 590	0.011 570				13.9568	13.958
3	2	13.966	0.003 043	0.003 063					13.964
1	1	13.967	0.048 880	0.048 880				13.9709	13.967
2	2	13.988	0.000 421	0.000 415					
2	1	14.018	0.062 790	0.062 720	14.034(8)	14.027		14.0202	14.015
1	0	14.078	0.020 050	0.020 080					
1	0	14.079	0.004 400	0.004 371					14.085
1	1	14.107	0.001 297	0.001 299					
0	1	14.108	0.001 571	0.001 568					
2	1	14.109	0.001 561	0.001 545					
1	0	14.120	0.034 950	0.034 950					14.126
1	2	14.124	0.000 962	0.000 964					
3	2	14.124	0.002 662	0.002 652					14.120
1	0	14.162	0.006 762	0.006 810					
2	2	14.176	0.002 315	0.002 313					14.173
1	0	14.256	0.033 870	0.033 840					14.263
1	2	14.267	0.000 045	0.000 045					
2	2	14.269	0.000 058	0.000 057					
3	2	14.271	0.000 224	0.000 222					
1	0	14.444	0.000 083	0.000 085					
1	0	14.593	0.000 027	0.000 027					

$j_K(\omega r/c)$ are spherical Bessel functions, and G_K is a gauge constant [21].

In general, a different choice of the gauge constant G_K leads to different expressions for the transition matrix elements. When the many-electron wave functions are exact solutions of the Dirac equation, the use of different forms for G_K matrix elements should lead to the same result. If the wave functions of the initial and final states are approximate solutions, the transition probability or oscillator strength may depend on G_K. Oscillator strengths for different gauge forms can be a reliable criterion for assessing the accuracy of the wave function.

After application of the Wigner-Eckart theorem Eq. (14) can be expressed as

$$A_K^{(e)}(B \to A) = 2\tilde{\alpha}\omega \frac{(2J_A+1)(2K+1)}{2J_B+1} \left| \frac{\langle \tilde{\alpha} | \mathbf{T}_{K\tilde{Q}}^{(e)} | \tilde{b} \rangle}{C^{J_A M_{\tilde{a}}}_{J_B M_{\tilde{b}}, K\tilde{Q}}} \right|^2, \tag{17}$$

where the $C^{J'M'}_{JM,KQ}$ is a Clebsh-Gordan coefficient and $\tilde{Q} = M_{\tilde{b}} - M_{\tilde{a}}$. Consequently, we have replaced the summations over magnetic sublevels in Eq. (14) by a single transition matrix element for particular projections $M_{\tilde{b}}$ and $M_{\tilde{a}}$. The final expression for A_K^e includes parameters that reflect the multiconfiguration and nonorthogonal character of the initial and final states. As a result we obtain

$$A_K^{(e)}(B\to A)=2\tilde{\alpha}\omega\frac{(2J_A+1)(2K+1)}{(2J_B+1)|C^{J_AM_{\tilde{a}}}_{J_BM_{\tilde{b}},K\tilde{Q}}|^2}\times\left|\sum_{\alpha\beta}(D_{\alpha\alpha}D_{\beta\beta})^{-1/2}\cdot D_{\alpha\beta}\cdot c_\alpha\cdot c_\beta\times\sum_{ij}^{N}(S^{-1})_{i,j}^{\alpha,\beta}\langle i|\mathbf{T}_{KQ}^{(e)}|j\rangle\right|^2, \quad (18)$$

where $(S^{-1})_{ij}^{\alpha,\beta}$ is the inverse of the matrix of overlap integrals between orbitals i and j; belonging to α and β determinants, respectively. $D_{\alpha\beta}$ is the determinant of the overlap matrix $(\hat{S})^{\alpha,\beta}$.

The single-orbital matrix element in Eq. (19) is given by

$$\langle i|\mathbf{T}_{KQ}^{(e)}|j\rangle=\delta_{Q,\mu_i-\mu_j}\frac{g^K(j_i\mu_i;j_j\mu_j)}{2K+1}\Bigg\{(k_i-k_j)\left[\sqrt{\frac{K}{K+1}}+G_K\right]I_{K+1}^{(+)}(i,j)+(L+1)\left[\sqrt{\frac{K}{K+1}}+G_K\right]\times I_{K+1}^{(-)}(i,j)-(k_i-k_j)\left[\sqrt{\frac{K+1}{K}}-G_K\right]\times I_{K-1}^{(+)}(i,j)+K\left[\sqrt{\frac{K+1}{K}}-G_K\right]I_{K-1}^{(-)}(i,j)+(2K+1)G_KR_K(i,j)\Bigg\}, \quad (19)$$

where the radial integrals $I_K^{(\pm)}(i,j)$ are given by

$$I_{K\pm1}^{(\pm)}(i,j)=\int_0^\infty dr[P_i(r)Q_j(r)\pm Q_i(r)P_j(r)]j_{K\pm1}(\omega r/c), \quad (20)$$

the coefficients $g^K(j_i\mu_i;j_j\mu_j)$ are relativistic Gaunt coefficients, and

$$R_K(i,j)=\int_0^\infty dr[P_i(r)P_j(r)+Q_i(r)Q_j(r)]V_K(r). \quad (21)$$

For the Coulomb gauge (G_K=0) we obtain the "velocity" form and for the gauge $[G_K=\sqrt{(K+1)/K}]$ we have "length" form of $\langle i|\mathbf{T}_{KQ}^{(e)}|j\rangle$.

The dimensionless oscillator strength is defined by

$$f_{A\to B}=\frac{m_ec^2}{2\tilde{\alpha}\omega^2}\frac{2J_B+1}{2J_A+1}A_K^{(e)}(B\to A), \quad (22)$$

where $A_K^{(e)}$ is expressed in s^{-1}, the transition wavelength λ is in Å, and m_e is the electron mass in kg.

III. RESULTS AND DISCUSSION

The Fe XIX lines in this study are due to transitions between the $1s^22s^22p^3\,3s$ or $3d$ excited levels and the $1s^22s^22p^4$ levels of the ground configuration. These transitions have attracted considerable attention from theory and experiment, thus allowing us to roughly compare our *ab initio* results with observations and predictions from Refs. [6,8,9,11]. Moreover, our calculations show numerous lines not found in any refereed publications.

The scale of the calculation is determined by the size of the Hamiltonian matrix $H_{\alpha,\alpha'}$ in the principal configuration space ($\mathcal{P}$), defined in Sec. II B. For Fe XIX calculation the configuration space ($\mathcal{P}$) includes CSFs constructed from the following atomic orbitals: $1s^22s^22p^q3s3p3d4s4p4d4f5s5p5d5f6s6p6d6f6g$ and $6h$. The size of the corresponding matrix $H_{\alpha,\alpha'}$ depends on the major configuration and the total angular momentum J. For example, the matrix to calculate energies of the relativistic $1s^22s^22p^33d$ configurations has about 2 500 000 $\times$ 2 500 000 elements, whereas the ground state configuration matrix includes only 288 400 $\times$ 288 400 matrix elements. We use the Davidson iterative diagonalization procedure to solve these matrices. The complimentary configuration space $\mathcal{Q}$ includes CSFs which give marginal contributions to the total energy. These CSFs are constructed from the higher excited orbitals such as $7s7p7d7f8s8p8d9s9p$ and $9d$ and their contribution to the CI expansion is calculated by second-order perturbation theory. In our computations all orbitals are divided into two groups, valence occupied $1s2s2p3s3p$ and $3d$ orbitals and virtual nonoccupied $4s4p4d4f5s5p5d5f6s6p6d\ldots$ up to $9d$ orbitals.

Oxygenlike Fe XIX has five levels in the ground $1s^22s^22p^4$ configuration, while the excited $1s^22s^22p^33s$ and $3d$ configurations have 10 and 35 levels, respectively. Tables II and III show the total energy and the value of the Breit and QED contributions for various levels of the ground and excited $1s^22s^22p^33s$ configuration of Fe XIX, respectively. These tables demonstrate the size of the QED and relativistic corrections. Similar orders of magnitude for these corrections for the levels of the $1s^22s^22p^33d$ configuration have been obtained.

The complete list of transitions from the excited $1s^22s^22p^33s$ and $3d$ levels to the levels of the ground configuration is given in Table IV. The first three columns of this table include wavelengths and oscillator strengths, in velocity and length forms, obtained in our calculation. Agreement between these two sets of oscillator strengths indicate that the uncertainty in the calculation is less then 1%. The next columns show wavelength results of EBIT measurements and HULLAC calculations [9], recommended NIST data [8], predictions by Gu [11], and by Bhatia *et al.* [6].

The overall agreement of our data with the most accurate theoretical [11] and semiempirical [6] predictions is good. In most cases the discrepancy is not more than a few 10^{-3} Å with a systematic shift of our wavelengths towards smaller values. We believe the difference between our data and that of Ref. [11] is due to the way we treat correlation effects. In our calculation a large number of dominant configurations are included in the CI expansion whereas Ref. [11] relies heavily on perturbation theory. Finally, we want to

emphasize the significance of our data due to their completeness that will help to identify the many features in the high-resolution spectra observed by the Chandra and XMM-Newton satellites.

ACKNOWLEDGMENTS

This work was supported in part by Smithsonian Institution.

[1] V. F. Bratzev, G. B. Deyneka, and I. I. Tupitsyn, Izv. Akad. Nauk SSSR, Ser. Fiz. **41**, 2655 (1977); [Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl.) **41**, 173 (1977)].
[2] S. A. Kotochigova and I. I. Tupitsyn, J. Phys. B **20**, 4759 (1987).
[3] I. I. Tupitsyn, V. M. Shabaev, J. R. Crespo Lopez-Urrutia, and I. Draganic, Phys. Rev. A **68**, 022511 (2003).
[4] S. A. Kotochigova, K. P. Kirby, N. S. Brickhouse, P. Mohr, and I. I. Tupitsyn, XDAP Conf. Proc. **774**, 161 (2005).
[5] B. C. Fawcett, At. Data Nucl. Data Tables **34**, 215 (1986).
[6] A. K. Bhatia, B. C. Fawcett, J. R. Lemen, H. E. Mason, and K. J. H. Phillips, Mon. Not. R. Astron. Soc. **240**, 421 (1989).
[7] T. Shirai, Y. Funatake, K. Mori, J. Sugar, W. L. Wiese, and Y. Nakai, J. Phys. Chem. Ref. Data **19**, 127 (1990).
[8] Yu. Ralchenko, F.-C. Jou, D. E. Kelleher, A. E. Kramida, A. Musgrove, J. Reader, W. L. Wiese, and K. Olsen, http://physics.nist.gov/asd3.
[9] G. V. Brown, P. Beiersdorfer, D. A. Liedahl, K. Widmann, S. M. Kahn, and E. J. Clothiaux, Astrophys. J., Suppl. Ser. **140**, 589 (2002).
[10] A. Bar-Shalom, M. Klapisch, and J. Oreg, J. Quant. Spectrosc. Radiat. Transf. **71**, 169 (2001).
[11] M. F. Gu, Astrophys. J., Suppl. Ser. **156**, 105 (2005).
[12] F. C. Smith and W. R. Johnson, Phys. Rev. **160**, 136 (1967).
[13] I. P. Grant, Adv. Phys. **19**, 747 (1970).
[14] V. A. Fock, *The Principles of Quantum Mechanics*, 2nd ed. (Nauka, Moskow, 1976).
[15] R. Szmykowski, J. Phys. B **30**, 825 (1997).
[16] I. P. Grant and H. M. Quiney, Phys. Rev. A **62**, 022508 (2000).
[17] I. I. Tupitsyn and A. V. Loginov, Opt. Spectrosc. **94**, 319 (2003).
[18] D. Kato, X.-M. Tong, H. Watanabe, T. Fukami, T. Kinugawa, C. Yamada, S. Ohtani, and T. Watanabe, J. Chin. Chem. Soc. (Taipei) **48**, 525 (2001).
[19] S. Kotochigova, P. J. Mohr, and B. N. Taylor, Can. J. Phys. **80**, 1373 (2002).
[20] A. I. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics* (Interscience, New York, 1965).
[21] I. P. Grant, J. Phys. B **7**, 1458 (1974).