Pecularities of spectroscopic properties of W^{24+}

Gediminas Gaigalas,[1,2,*] Zenonas Rudzikas,[1] Erikas Gaidamauskas,[1] Pavel Rynkun,[2] and Andrius Alkauskas[2]

[1]*Vilnius University, Institute of Theoretical Physics and Astronomy, A. Goštauto 12, LT-01108, Vilnius, Lithuania*

[2]*Department of Physics, Vilnius Pedagogical University, Studentų 39, Vilnius LT-01108, Lithuania*

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We aim at demonstrating the feasibility of accurate theoretical studies of atoms and ions having complex electronic configurations, open f shell included, by combining the second quantization method in coupled tensorial form with a quasispin technique, leading to triple tensors (in orbital, spin, and quasispin spaces). The large-scale nonrelativistic and relativistic calculations of the 977 lowest energy levels of W^{24+}, accounting for correlation, relativistic, and quantum electrodynamics effects, demonstrate the high efficacy of the methods used. The accuracy of the LS- and jj-coupling schemes is discussed as well. The wavelengths of electric dipole transitions, their line strengths and transition probabilities, as well as the lifetimes of some lowest excited levels are also calculated. The authors hope that the success in theoretical studies of such complex ions will stimulate relevant experimental research, encouraging yet further progress in the theory.

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Tungsten (W) is planned to be used as a plasma wall material in future tokamaks, such as ITER and DEMO. Therefore, a detailed analysis of its thermonuclear plasma spectra, the impurities within it, and a knowledge of the large number of its free-ion spectroscopic parameters are needed. For this purpose it is important to perform a comprehensive theoretical modeling of the atomic structure of various tungsten ions. Such ions, having simple electronic configurations of open shells (up to highly ionized atoms), have been studied both experimentally and theoretically fairly completely, but this is not the case for ions, having an open f shell. It has been extremely difficult or even impossible to perform such calculations for tungsten ions with its open f shell owing to the large number of atomic states. Indeed, accurate experimental or theoretical spectroscopic data for such ions are sparse [1,2]. In this Brief Report we present the results of the large-scale multiconfiguration calculations of the energetically lowest W^{24+} configurations, demonstrating the feasibility of such studies.

We used different *ab initio* methods, namely the multiconfiguration Hartree-Fock (MCHF) and multiconfiguration Dirac-Fock (MCDF) approaches, taking into account relativistic and QED corrections [3]. The nonrelativistic configuration interaction method was used to include the Breit-Pauli approximation (BP) and the relativistic configuration interaction (RCI) method was used to include the transverse Breit interaction (B) at the low-frequency limit (describing the transversely polarized photon contributions to the electron-electron interactions in Coulomb gauge) and the QED corrections (including self-energy and vacuum polarization) [4,5]. MCDF calculations were performed with the GRASP2K relativistic atomic structure package [4,6] in which for calculations of spin-angular parts of matrix elements the second quantization method in coupled tensorial form and the quasispin technique [3] were adopted. This allowed us to achieve the breakthrough in the field, to essentially increase the efficacy and the speed of the calculations, opening the possibilities to consider extremely complex electronic configurations.

In case of the MCDF expansions of the even and odd Atomic state function (ASF) for the energy spectrum calculations we used a multireference (MR) set of configuration state functions (CSFs) based on the $[\mathrm{Kr}]4d^{10}4f^4$ and $[\mathrm{Kr}]4d^{10}4f^35p$ even as well as $[\mathrm{Kr}]4d^{10}4f^35s$ and $[\mathrm{Kr}]4d^94f^5$ odd configurations. The even and odd ASFs were calculated independently. The state functions of these four configurations form the basis for the zero-order wave function (MR set). The energy functional on which the orbitals were optimized was defined according to an extended optimal level (EOL) scheme [4], where a linear combination of atomic states, corresponding to the lowest two $J = 0, \ldots, 8$ states, were used (with the same scheme being used for the even and odd states). Admixed CSFs were obtained from single substitutions from all open-shell orbitals to an increasing active set (AS) of orbitals. The AS is labeled by an integer n and includes s, p, and d orbitals with principal quantum numbers up to n and f orbitals up to $n-1$. For example, the active set $AS_{n=6}$ contains s, p, and d orbitals with principal quantum number up to 6 and f orbitals up to $n = 5$. The active sets were successively extended to $n = 7$. At all steps only new orbitals were optimized.

Figure 1 displays the computed energies of the 977 lowest levels of W^{24+} belonging to $[\mathrm{Kr}]4d^{10}4f^4$ (107 levels), $[\mathrm{Kr}]4d^{10}4f^35s$ (82 levels), $[\mathrm{Kr}]4d^{10}4f^35p$ (242 levels), and $[\mathrm{Kr}]4d^94f^5$ (incomplete, 546 levels) configurations. The results presented are obtained in the both nonrelativistic and relativistic approaches. In the nonrelativistic case the largest scale MCHF and configuration interaction approximation as well as the ATSP package [7] were used. Figure 1 indicates that both (nonrelativistic and relativistic) approximations lead to a similar general picture of the energy spectra of the $[\mathrm{Kr}]4d^{10}4f^4$ and $[\mathrm{Kr}]4d^{10}4f^35s$ configurations. However, the detailed analysis of the numerical data reveals the essential differences in the structure of their energy spectra. Thus, for studies of the energy spectra, fine structure, electron transition probabilities, lifetimes, etc., of such ions, one must use already at the very beginning the relativistic approach.

The main peculiarity of the W^{24+} ion consists in the uniqueness of its ground configuration, containing the only open f shell, namely, $4f^4$. As we see from the calculations, the lowest excited state of this ion is $4f^35s$. Normally,

*Gediminas.Gaigalas@tfai.vu.lt

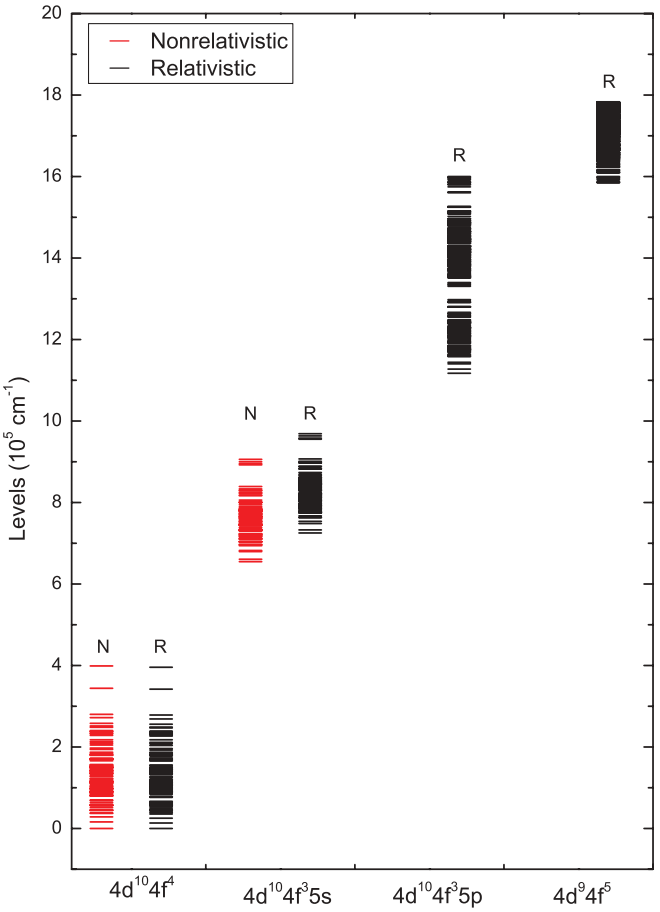

FIG. 1. (Color online) Configurations of W^{24+} in different approaches [MCHF + BP in red (N) and MCDF + B + QED in black (R)] with AS_7 expansion (single excitation).

electric dipole electronic transitions are allowed between the first excited and ground configuration. As a rule they are the strongest. In our case, however, such transitions are of octopole character. Quite unique are also the electronic transitions from the higher excited configuration to the ground configuration (quadrupole for $4f^35p$–$4f^4$) or between the excited configurations (e.g., two-electron transitions).

The evaluation of the suitability of the LS and jj couplings for the classification of energy spectra is performed using the methodic described in [8,9].

Table I presents the square of the largest coefficient averaged over the states (P_s) in the MCHF + BP and in the MCDF + B + QED approaches. In the first case the energy levels are characterized by the quantum numbers of the LS coupling, whereas in the second one they are characterized by jj coupling. The larger the P_s value, the better is the coupling scheme. In the ideal case P_s may reach 1. We were unable to find a P_s value for [Kr]$4d^{10}4f^35p$. It follows from Table I that both coupling schemes are almost equally unsuitable and for the atomic states of these configurations it is important to use the intermediate coupling approximation. However, configuration mixing between investigated nonrelativistic configurations is relatively week. Therefore, for the electric dipole ($E1$) electronic transitions, instead of the exact selection rules $\Delta J = 0, \pm 1$ ($J = J' \neq 0$), $\Delta l = \pm 1$, the selection rules for the other quantum numbers are approximate.

TABLE I. A square of the largest coefficient averaged over the states (P_s) in the MCHF + BP (LS-coupling) and in the MCDF + B + QED (jj-coupling) approaches.

	P_s	
Configuration	LS coupling	jj coupling
[Kr] $4d^{10}4f^4$	0.53	0.56
[Kr] $4d^{10}4f^35s$	0.54	0.52
[Kr] $4d^{10}4f^35p$		0.46

The electric dipole ($E1$) transitions have the largest probabilities. That is why one of the goals of this Brief Report is to study their peculiarities in W^{24+}. We can see from Fig. 1 that the $E1$ transitions are allowed only between the levels of the excited configurations [Kr]$4d^{10}4f^35p$ and [Kr]$4d^{10}4f^35s$. For the calculations of the $E1$ transitions between initial even [Kr]$4d^{10}4f^35p$ and final odd [Kr]$4d^{10}4f^35s$ configurations we used the single reference (SR) set. The even and odd ASFs were calculated independently. The $E1$ transition data (wavelengths, transition probabilities, and line strengths) were calculated using the biorthogonal orbital transformations [10].

In Table II we present the most probable transition probabilities (exceeding 6×10^{10} s^{-1}) for spontaneous emission and line strengths of $E1$ transitions in both Babushkin (length) and Coulomb (velocity) gauges.

Figure 2 presents the distribution of the transition probabilities for spontaneous emission A in s^{-1} of electric dipole transitions among the levels of [Kr]$4d^{10}4f^35p$ and [Kr]$4d^{10}4f^35s$ configurations in the Babushkin gauge with respect to their wavelengths. As seen, there are some transitions with probabilities significantly higher than others. The

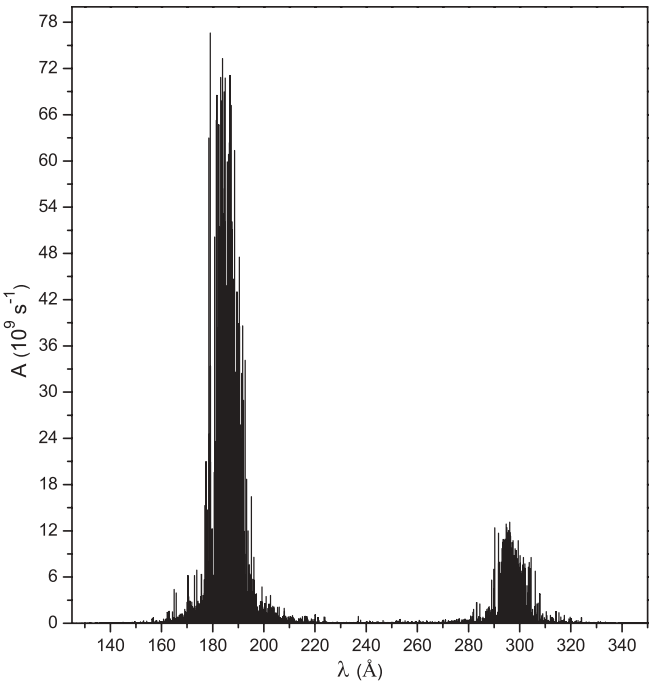

FIG. 2. Theoretical $E1$ transition emission probabilities in the MCDF + B + QED approach with AS_7 atomic state function expansion (single excitation) in Babushkin gauge.

TABLE II. Calculated wavelengths λ (in 10^2 Å), transition probabilities A (in 10^{10} s^{-1}), and line strengths S for the most probable (exceeding 6×10^{10} s^{-1}) electric dipole transitions among the levels of $[Kr]4d^{10}4f^3 5p$ and $[Kr]4d^{10}4f^3 5s$ configurations. The notation w means position of level among the levels with the same total angular momentum quantum number J, and J P stands for the total angular momentum quantum number J and parity P (classification of the levels in jj coupling).

Upper			Lower			λ	A (10^{10} s^{-1})		S	
Configuration	J P	w	Configuration	J P	w	(10^2 Å)	A_C	A_B	S_C	S_B
$4f_-^3(J=\frac{3}{2})5p$	0+	9	$4f_-^3(J=\frac{3}{2})5s$	1−	1	1.872 645	6.722	6.942	0.218	0.225
$4f_-^2(J=2)4f(J_{12}=\frac{3}{2})5p$	0+	10	$4f_-^2(J=2)4f(J_{12}=\frac{3}{2})5s$	1−	2	1.885 351	6.135	6.300	0.203	0.208
$4f^3(J=\frac{5}{2})5p$	1+	29	$4f^3(J=\frac{5}{2})5s$	2−	12	1.816 095	6.849	7.018	0.607	0.622
$4f_-4f^2(J=0)5p$	1+	30	$4f_-4f^2(J=0)5s$	2−	13	1.790 459	7.660	7.874	0.651	0.669
$4f^3(J=\frac{7}{2})5p$	2+	50	$4f_-^2(J=0)4f(J_{12}=\frac{7}{2})5s$	3−	12	1.814 150	6.525	6.723	0.962	0.991
$4f^3(J=\frac{7}{2})5p$	2+	52	$4f^3(J=\frac{7}{2})5s$	3−	13	1.785163	6.296	6.493	0.884	0.912
$4f_-4f^2(J=0)5p$	4+	59	$4f_-4f^2(J=0)5s$	3−	14	1.823 401	6.468	6.621	1.742	1.783
$4f_-^3(J=\frac{9}{2})5p$	3+	26	$4f_-^3(J=\frac{9}{2})5s$	4−	1	1.844 713	6.896	7.155	1.496	1.552
$4f^3(J=\frac{7}{2})5p$	5+	48	$4f^3(J=\frac{7}{2})5s$	4−	14	1.830 873	7.085	7.259	2.361	2.419
$4f_-^3(J=\frac{9}{2})5p$	6+	22	$4f_-^3(J=\frac{9}{2})5s$	5−	1	1.861 758	6.084	6.233	2.519	2.581
$4f_-4f^2(J=2)(J_{12}=\frac{9}{2})5p$	6+	39	$4f_-4f^2(J=2)(J_{12}=\frac{9}{2})5s$	5−	12	1.836 273	6.780	6.946	2.693	2.760
$4f_-^2(J=4)4f(J_{12}=\frac{11}{2})5p$	7+	14	$4f_-^2(J=4)4f(J_{12}=\frac{11}{2})5s$	6−	1	1.865 237	6.235	6.358	2.996	3.054
$4f_-4f^2(J=6)(J_{12}=\frac{13}{2})5p$	8+	12	$4f_-4f^2(J=6)(J_{12}=\frac{13}{2})5s$	7−	1	1.867 704	6.589	6.698	3.602	3.662
$4f_-4f^2(J=6)(J_{12}=\frac{15}{2})5p$	9+	4	$4f_-4f^2(J=6)(J_{12}=\frac{15}{2})5s$	8−	1	1.867 316	7.108	7.202	4.340	4.397
$4f_-^2(J=4)4f(J_{12}=\frac{15}{2})5p$	9+	5	$4f_-^2(J=4)4f(J_{12}=\frac{15}{2})5s$	8−	2	1.848 967	7.075	7.194	4.194	4.264
$4f_-4f^2(J=6)(J_{12}=\frac{17}{2})5p$	10+	3	$4f_-4f^2(J=6)(J_{12}=\frac{17}{2})5s$	9−	1	1.838 271	7.329	7.458	4.718	4.802

transition probabilities considered are in the time interval of 10^{+2}–10^{+10} s^{-1}. The largest A are localized in two wavelength intervals. The most probable transitions are localized in the 170–198 Å domain. Transition probabilities, localized in the second domain (285–310 Å), are generally lower. These domains are of interest for thermonuclear plasma diagnostics.

In Table III the lifetimes τ of the 10 lowest excited levels belonging to the configuration $[Kr]4d^{10}4f^3 5p$ are presented in both Babushkin (length) and Coulomb (velocity) gauges [3,11]. The good agreement between the two gauges is seen. The lifetimes of the rest (higher) energy levels τ are similar to those presented in Table III and are of the order of 10^{-11} s.

TABLE III. Calculated lifetimes τ (in 10^{-11} s) of the 10 lowest excited levels belonging to the configuration $[Kr]4d^{10}4f^3 5p$. The notation w means positions of a level among the levels with the same total angular momentum quantum number J, and J P stands for the total angular momentum quantum number J and parity P (classification of the levels in jj coupling).

Levels			τ (10^{-11} s)	
Configuration and coupling scheme	J P	w	τ_C	τ_B
$4d_-^4 4d^6 4f_-^3(J=\frac{9}{2})\,5p_-$	5+	15	5.843	5.851
$4d_-^4 4d^6 4f_-^3(J=\frac{9}{2})\,5p_-$	4+	20	5.634	5.533
$4d_-^4 4d^6 4f_-^2(J=4)\,4f(J_{12}=\frac{11}{2})\,5p_-$	6+	14	5.755	5.727
$4d_-^4 4d^6 4f_-^2(J=4)\,4f(J_{12}=\frac{11}{2})\,5p_-$	5+	16	5.698	5.582
$4d_-^4 4d^6 4f_-^3(J=\frac{3}{2})\,5p_-$	2+	18	5.788	5.756
$4d_-^4 4d^6 4f_-4f^2(J=6)\,(J_{12}=\frac{13}{2})\,5p_-$	7+	8	5.730	5.679
$4d_-^4 4d^6 4f_-^3(J=\frac{3}{2})\,5p_-$	1+	8	5.747	5.670
$4d_-^4 4d^6 4f_-4f^2(J=6)\,(J_{12}=\frac{13}{2})\,5p_-$	6+	15	5.654	5.512
$4d_-^4 4d^6 4f_-^2(J=4)\,4f(J_{12}=\frac{9}{2})\,5p_-$	5+	17	5.761	5.718
$4d_-^4 4d^6 4f_-^2(J=4)\,4f(J_{12}=\frac{9}{2})\,5p_-$	4+	21	5.725	5.631

Because of the absence of relevant experimental results it is impossible to present accurate error estimates for each entry. However, there are indirect hints that suggest fairly high precision of the approach and results obtained. These include the high accuracy of such calculations for simpler configurations, the convergency of the accounting for correlation effects, comparison of nonrelativistic (but accounting for relativistic corrections) and relativistic calculations, and calculation of complex systems such as Cm^{4+} [12], Am^{3+} [12], eka-thorium [13], and Ra [14] in the same approach with the same programs.

The agreement between the two gauges is within 2.5% for strong $E1$ transitions. For weak transitions the accuracy is lower. The weakness of a transition frequently comes out as a result of violations of selection rules or as cancellation between a number of large contributions or between different parts of the radial transition integrals. A small imbalance due to correlation effects may thus change the calculated transition probabilities dramatically. But the general wisdom is that values in the Babushkin gauge are the more accurate ones. The results of Table II show that for every J value of the upper or lower configurations there are highly probable transitions.

We also investigated the gauge dependence of the transition rates (Fig. 3). In the general case it has a parabolic form with respect to the gauge parameter (G axis). This dependence may also be used to evaluate the accuracy of the results. The more accurate is the wave function, the closer is the parabola to a straight line. These results show that the accuracy due to the correlation contribution to the transition

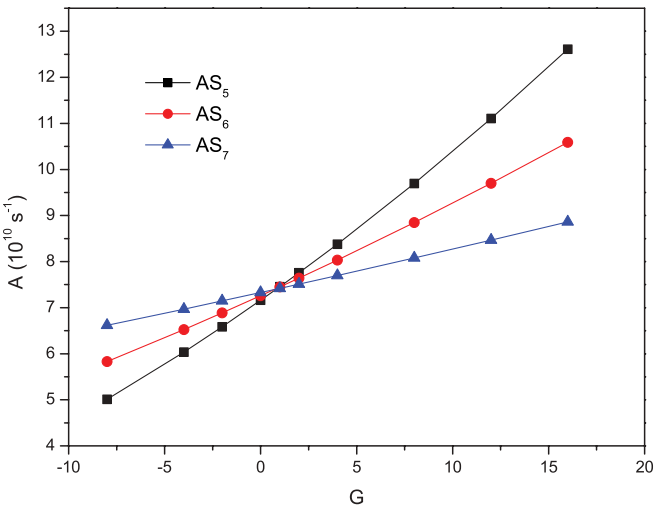

FIG. 3. (Color online) The gauge dependence (G) of the ($w = 3$, $J^+ = 10^+$) $\rightarrow$ ($w = 1$, $J^- = 9^-$) $E1$ transition probability for the different restricted active space calculations in the MCDF + B + QED approach.

rates [to the G-independent part of the A(G)] is on average 4.5%.

The results of this Brief Report indicate that by taking into account modern methods considered for the spin-angular parts of the matrix elements of the energy operator [3,15] combined with the newest versions of computer codes for atomic calculations one is in a position to study most complex electronic configurations of atoms and ions, highly charged atoms included, and to obtain fairly accurate data on energy spectra, transition probabilities, lifetimes of excited levels, and other spectroscopic parameters. We hope that the success in theoretical studies of such complex ions will stimulate relevant experimental research, encouraging in such a way the further progress in the theory. In the particular case of the W^{24+} ion it would be important to study magnetic dipole and electric quadrupole electron transitions inside the ground configuration [Kr]$4d^{10}4f^4$, as well as the electric octopole and magnetic quadrupole electron transitions between the first excited configuration [Kr]$4d^{10}4f^35s$ and ground configuration [Kr]$4d^{10}4f^4$, because electric dipole transitions are strictly forbidden. Some of these transitions may be useful for the diagnostics of thermonuclear plasma.

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[1] T. Pütterich, R. Neu, R. Dux, A. D. Whiteford, and M. G. O'Mullane, Plasma Phys. Controlled Fusion **50**, 085016 (2008).
[2] A. E. Kramida and T. Shirai, At. Data Nucl. Data Tables **95**, 305 (2009).
[3] Z. Rudzikas, *Theoretical Atomic Spectroscopy*, 2nd ed. (Cambridge University Press, New York, 2007).
[4] P. Jönsson, X. He, C. F. Fischer, and I. Grant, Comput. Phys. Commun. **177**, 597 (2007).
[5] B. J. McKenzie, I. P. Grant, and P. H. Norrington, Comput. Phys. Commun. **21**, 233 (1980).
[6] C. F. Fischer, G. Gaigalas, and Y. Ralchenko, Comput. Phys. Commun. **175**, 738 (2006).
[7] C. F. Fischer, G. Tachiev, G. Gaigalas, and M. Godefroid, Comput. Phys. Commun. **176**, 559 (2007).
[8] Z. B. Rudzikas and J. V. Čiplys, Phys. Scr. T **26**, 21 (1989).
[9] T. Žalandauskas, G. Gaigalas, and Z. Rudzikas, Nucl. Instrum. Methods Phys. Res. B **235**, 149 (2005).
[10] J. Olsen, M. R. Godefroid, P. Jönsson, P. A. Malmqvist, and C. F. Fischer, Phys. Rev. E **52**, 4499 (1995).
[11] K. Dyall, I. Grant, C. Johnson, F. Parpia, and E. Plummer, Comput. Phys. Commun. **55**, 425 (1989).
[12] G. Gaigalas, E. Gaidamauskas, Z. Rudzikas, N. Magnani, and R. Caciuffo, Phys. Rev. A **79**, 022511 (2009).
[13] G. Gaigalas, E. Gaidamauskas, Z. Rudzikas, N. Magnani, and R. Caciuffo, Phys. Rev. A **81**, 022508 (2010).
[14] J. Bieroń, G. Gaigalas, E. Gaidamauskas, S. Fritzsche, P. Indelicato, and P. Jönsson, Phys. Rev. A **80**, 012513 (2009).
[15] G. Gaigalas, Z. Rudzikas, and C. F. Fischer, J. Phys. B **30**, 3747 (1997).