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Radiative decay from doubly to singly excited states of He via generalization of Laguerre-type orbitals: A non-orthogonal formalism*

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By taking full account of the non-orthogonality of the orbitals between the low-lying doubly excited states $^1P^o$ and the singly excited states $^1S^e$ and $^1D^e$ of He, the corresponding radiative decay rates have been investigated theoretically via analytic generalized Laguerre-type atomic orbitals at a nearly numerical multi-configuration self-consistent field accuracy in a general non-orthogonal configuration interaction scheme. From these rates, we calculate the VUV photon emission and metastable atom spectra, and both are found to be in good qualitative agreement with recent excellent measurements. We obtain, successfully, the enhancement of the VUV photon spectrum, experimentally observed at the energy of (2s4p-4s2p)/(2p,3d) $^1P^o$ as compared with other nearby lying states. The mechanism proposed by Odling-Smee *et al* is verified, implying that taking appropriate account of the overlap existing between orbitals of the low-lying doubly excited and singly excited states (especially important for the compact orbitals) can reveal basic physical dominant mechanism and is crucial in understanding these spectra.

Keywords: doubly excited states, singly excited states, analytic basis functions, non-orthogonality formalism
PACC: 3120A, 3120T, 3270C

1. Introduction

Over the last few decades, a detailed understanding of He doubly excited states, which is fundamental for understanding electron correlation, has been achieved through the advances of synchrotron radiation sources,[1] experimental improvement of spectral resolution[2] and various theoretical approaches.[3−7] The radiative decay of these states, however, has been tacitly neglected, with autoionization considered to be the main decay mechanism, until the recent experiments of Odling-Smee *et al*[8] and Rubensson *et al.*[9] There was shown an unexpected feature: an enhancement of the VUV photon yield at the energy of (2s4p-2p4s)/(2p3d) $^1P^o$ (see Fig.3), compared with both the lower lying 2s3p-2p3s and the higher lying (2s5p-2p5s)/(2p4d) (and even higher lying, which give even smaller yields). There are two theoretical approaches to this phenomenon, one is Liu *et al*'s approach,[10] in which B-spline basis functions are used in calculation and a good qualitative agreement between the calculation and measurement of metastable atom yield has been achieved, but the VUV photon yield was predicted to have a maximum at the energy of (2s5p-2p5s)/(2p4d) instead, and the other is Zitnik *et al*'s approach,[11] in which the calculation is performed by large expansions in single configurations composed of orthogonal hydrogenlike helium orbitals and gives a maximum at (2s4p-2p4s)/(2p3d). Liu *et al*[10] attributed their discrepancy to experimental inconsistencies, but these experimental values at least agree with other relevant data obtained from all other existing experiments (see Refs.[11–13] and references therein). Since Zitnik *et al*'s[11] results are also in agreement with other experimental data, in our opinion, the measurements concerning the above enhancement are consistent within an experimental error. Therefore, we think that it is worth examining the disputed enhancement by using other technique based on analytic multi-configuration global energy

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minimization, via analytic, accurate, but concise and practical orbitals.

We have developed a method with analytic, semiorthogonal[14,15] basis functions, which satisfactorily approximates the accuracy of numerical multiconfiguration self-consistent field (NMCSCF) and is one of the most accurate methods. Therefore these orbitals are concise and clearly interpretable. We apply them to doubly excited states of He below the 2nd ionization threshold and, in addition, we develop a general non-orthogonal formalism of radiative decay. Thus we have successfully achieved good qualitative agreement for both the metastable atom and the VUV photon spectra with the above measurements,[8,9] in favour of Zitink *et al*'s results;[11] therefore we strongly support the proposition of Odling-Smee *et al* in Ref.[8] that the radiative decay of the energetically narrow 2pnd states, preferentially to 1smd ($n \approx m$), is essential to understanding the observed VUV spectra. It also suggests that taking account of the inherent overlap (non-orthogonality) between the orbitals of doubly and singly excited states is necessary in calculating these radiative transitions.

2. Theory

The spherical tensor operator for electric dipole transitions, after expanding the ith electron's position operator in angular and radial parts, is

$$T^1_m = \sum_{i=1}^{n} Y_{1m}(i) r(i), \tag{1}$$

where $Y_{1m}(i)$ ($m = 0, \pm 1$) are spherical harmonics, and $r(i)$ is the distance of electron from the nucleus.[16] In the LS coupling approximation, the multiplet strength for an electric dipole transition between an initial state γSL and a final state $\gamma' SL'$ is given by[17]

$$S(\gamma SL, \gamma' SL') = (2S+1) \sum_{m, M_J, M'_J} |\langle \gamma LSJM_J | T^1_m | \gamma' L' SJ' M'_J \rangle|^2 = (2S+1) |\langle \gamma L || T^1 || \gamma' L' \rangle|^2, \tag{2}$$

where γ represents the electron configuration and all additional quantum numbers needed to completely specify the state.

In the multi-configuration approximation the wavefunction is given by an expansion in terms of Slater determinants, i.e. for an N-electron system, the wavefunctions of the initial and final states, having $N_{\rm c}$ and $N'_{\rm c}$ configurations out of $N_{\rm d}$ and $N'_{\rm d}$ Slater determinants D_i and D'_j respectively, are

$$\Psi(\gamma SL) = \sum_{p=1}^{N_{\rm c}} c_p \Gamma_p \quad \text{with} \quad \Gamma_p = \sum_{i=1}^{N_{\rm d}} f_{ip} D_i, \quad D_i = |\alpha_{1i}, \ldots, \alpha_{ki}, \ldots, \alpha_{Ni}|, \tag{3}$$

and

$$\Psi'(\gamma' SL') = \sum_{q=1}^{N'_{\rm c}} c'_q \Gamma'_q \quad \text{with} \quad \Gamma'_q = \sum_{i=1}^{N'_{\rm d}} f'_{i,q} D'_j, \quad D'_j = |\alpha'_{1j}, \ldots, \alpha'_{kj}, \ldots, \alpha'_{Nj}|, \tag{4}$$

where c_p and c'_q are the configuration coefficients, $f_{i,p}$ and $f'_{j,q}$ are the LS terms coefficients, a_{ki}, a'_{kj} are the spin-orbitals for the initial and the final states. In a_{ki} and a'_{kj}, we use the orbitals that we have developed in the following form:[14,15]

$$\langle r | n, l, m \rangle = A_{n,l,m} L_{n,l}(\{g\}, r, z_{n,l}, b_{n,l}, q_{n,l}) Y_{l,m}(\theta, \varphi), \tag{5}$$

where $A_{n,l,m}$ is a normalization constant and $Y_{l,m}(\theta, \varphi)$ are the spherical harmonics. The generalized, variationally optimized, Laguerre-type functions, that we proposed, are (in a.u.)

$$\begin{aligned} L_{n,l}(\{g\}, r, z_{n,l}, b_{n,l}, q_{n,l}) = & \sum_{k=0}^{n-l-1} c_k(n, l, z_{n,l}) g_k(n, l, \{z_{i,l}, b_{i,l}, q_i\}_{i=1}^{n}) r^{l+k} \\ & \times \exp(-z_{n,l} r/n) + b_{n,l} \exp(-q_{n,l} z_{n,l} r/n) \delta_{1,0}, \end{aligned} \tag{6}$$

where c_k are the associated Laguerre-polynomial coefficients and the g_k factors are a function of $z_{n,l}$, allowing the orthogonalization to lower-n orbitals of any known state, either ground (g) or excited (e). (For example, $2s_e$ can be orthogonalized to either $1s_e$ or $1s_g$, as desired). The parameters $z_{n,l}$ describing the extent of the orbitals are determined variationally from a (non-linear) minimization of the desired root of the secular equation.

In a general non-orthogonal formalism, the reduced matrix elements are

$$\langle \gamma L||T^1||\gamma' l'\rangle = \sum_{p,q=1}^{N_c,N_{c'}} \sum_{i,j=1}^{N_d,N_{d'}} c_p c'_q f_{pi} f'_{qj} \langle D_i||T^1||D'_j\rangle, \tag{7}$$

where

$$\langle D_i||T^1||D'_j\rangle = \frac{1}{\sqrt{D_{aa}D_{a'a'}}} \sum_{ki,kj=1}^{N} \langle a_{ki}||Y^1 r||a'_{kj}\rangle D_{aa'}(a_{ki}, a'_{kj}). \tag{8}$$

Here $D_{aa'}(a_{ki}, a'_{kj})$ is the cofactor of the element $\langle a_{ki}|a'_{kj}\rangle$ in the determinant $D_{aa'} = \det|\langle a_1|a'_1\rangle\langle a_2|a'_2\rangle \ldots \langle a_n|a'_N\rangle|$, and $D_{aa'}$, $D_{a'a'}$ are similar normalization factors.[18] Equation (8) holds generally for non-orthogonal orbitals between the initial and the final states. The one-electron reduced matrix elements are given by

$$\begin{aligned}\langle a_{ki}||Y^1 r||a'_{kj}\rangle \equiv\ & \langle nl||Y^1 r||n'l'\rangle \\ =\ & \langle l||Y^1||l'\rangle\langle nl|r|n'l'\rangle,\end{aligned} \tag{9}$$

where

$$\langle nl|r|n'l'\rangle = \int R_{nl} R_{n'l'} r^3 \mathrm{d}r, \tag{10}$$

and R_{nl} and $R_{n'l'}$ are the orbital radial functions [see Eq.(6)], and, by the properties of the $3j$-symbol,

$$\langle l||Y^1||l'\rangle = \pm\sqrt{\max(l,l')}\delta_{l',l\mp1}. \tag{11}$$

Then the radiative decay rate from the state γSL with energy E, to the state $\gamma' SL'$ with energy E' is given by[19]

$$A(\gamma SL, \gamma' SL') = \frac{4[\alpha(E'-E)]^3}{3g} S(\gamma SL, \gamma' Sl'), \tag{12}$$

where α is the fine structure constant ($\alpha = e^2/(\hbar c) = 1/137$), and g is the statistical weight for the initial state (for the LS coupling, $g = (2L+1)(2S+1)$).

3. Initial and final states

We treat the doubly excited (e) states (ns $n'l'$) of $^1P^o$ symmetry as bound states. According to the Eckart theorem,[20] these states must be orthogonal to all lower lying singly (s) excited states of $^1P^o$ symmetry, i.e. $\langle ns n'l'|1s_s n''p_s\rangle = 0$. In calculating various singly excited states ($1s_s n''p_s$), we have observed that the orbital effective charges z_{1s_s} are at most 2.003 a.u., tending to 2.000 a.u. as $n'' \to \infty$. Therefore, in order to avoid variational collapse, we keep 2s orthogonal to $1s_s$ with $z_{1s_s} = 2.003$, and all other ns orthogonal to the 2s. This approximation leads to energy values comparable with those in the literature[21–23] (Table 1). We have employed the 10-dimensional 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 5s, 5p basis space and we varied them according to the desired nth root of the secular equation, following the Hylleraas–Undheim–MacDonald (HUM) theorem.[24] Since our orbitals resemble NMCSCF functions accurately enough, this basis set is adequate. We identify each state by using their dominant configurations. Thus, if $2n^{\pm}$ denote $2sn\mathrm{p}\pm2pn\mathrm{s}$, then the optimized lowest nine roots lead to the 2s2p, $2n^+$, $2n^-$, $n = 3, 4, 5$ and 2p3d and 2p4d states. Their energies compare fairly well with those in the literature (cf. Table 1), though a strict comparison should be made for the resonance (complex) energies. (Treating the states as bound states[21–23] compared to treating them as resonance states,[25–31] flips the energy between 24^- and 2p3d, as well as between 25^- and 2p4d, by 0.001–0.006 a.u.) In all these states, the root-mean square (RMS) spatial extent ($\sqrt{\langle r^2\rangle}$) of the $n = 2$ shell is ≈ 3 a.u., and those of $2n^-$, n= 3, 4, 5 shells are around 9, 18, and 24 a.u. respectively, while for 2p3d, and 2p4d they are 14 and 28 a.u., which are reasonable.

Table 1. A comparison of energies (-E in atomic units) for the He doubly excited $^1P^{\rm o}$ sequence.

State	Main configurations	This work	Ref.[21]	Ref.[22]	Ref.[23]
22+	0.94 [2s2p] − 0.30 [2p3d] + ⋯	0.6915	0.6910	0.6883	0.6886
23+	0.63 [2p3s] + 0.52 [2s3p] + ⋯	0.5636	0.5637	0.5629	0.5637
24+	0.74 [2p4s] + 0.65 [2s4p] + ⋯	0.5325	0.5335	0.5338	0.5343
25+	0.70 [2p5s] + 0.69 [2s5p] + ⋯	0.5198	0.5205	0.5212	0.5199
23-	0.70 [2s3p] − 0.66 [2p3s] + ⋯	0.5970	0.5971	0.5967	0.5971
24-	0.74 [2s4p] − 0.60 [2p4s] + ⋯	0.5467	0.5468	0.5466	0.5475
25-	0.92 [2s5p] − 0.26 [2p5s] + ⋯	0.5273	0.5272	0.5212	0.5280
2p3d	0.88 [2p3d] − 0.37 [2s3p] + ⋯	0.5456	0.5463	0.5452	0.5471
2p4d	0.59 [2p4d] + 0.51 [2p3s] + ⋯	0.5261	0.5269	0.5212	0.5240

The singly excited states 1sns $^1S^{\rm e}$ and 1snd $^1D^{\rm e}$ are obtained directly via the HUM theorem[24] by demanding that all orbitals be orthogonal to each other. Their energies are comparable quite well with those in the literature[32,33] (see Table 2). In all these states, the $n = 1$ shell has RMS spatial extent ≈ 1 a.u., and the $n = 2$, 3, 4, 5 shells around 5, 11, 23 and 38 a.u. respectively. Thus, the orbital overlaps between the doubly and singly excited states are not negligible (see Fig.1). Consequentially, the general non-orthogonal treatment of them is needed.

Table 2. A comparison of energies (-E in atomic units) for He singly excited states $^1S^{\rm e}$ and $^1D^{\rm e}$.

State	This work	Ref. [32]
1s1s	2.9030	2.9036
1s2s	2.1460	2.1460
1s3s	2.0611	2.0613
1s4s	2.0335	2.0336
1s5s	2.0211	2.0212
1s3d	2.0556	2.0556
1s4d	2.0313	2.0313
1s5d	2.0200	2.0200

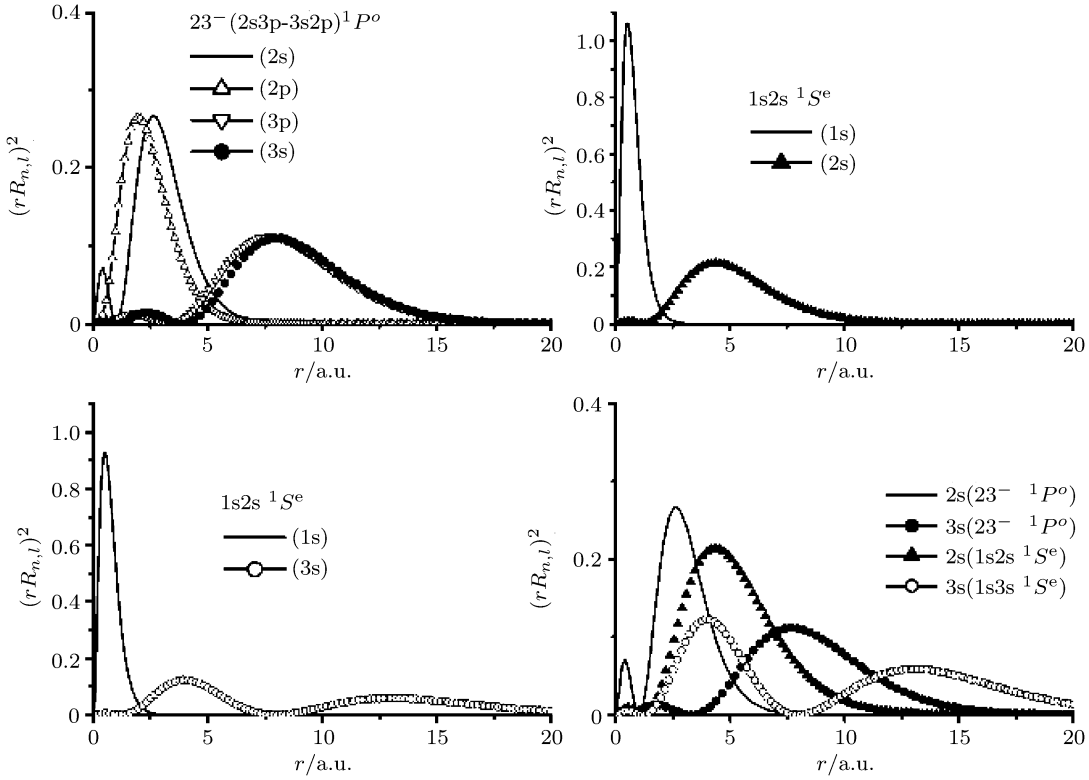


Fig.1. Our calculated orbitals of doubly excited state He (23⁻) $^1P^{\rm o}$ and singly excited (1s2s) and (1s3s) $^1S^{\rm e}$. The overlap between the 3s orbital of the doubly excited (23⁻) and the 2s and 3s orbitals of the singly excited states is large.

4. VUV photon and metastable atom yield calculation

As indicated in Fig.2, the one-step radiative decay of doubly excited states can proceed either directly to the ground state, producing a VUV photon, or to 1s2s $^1S^e$ state, producing a VUV photon and a metastable atom. Radiative decays into other 1sns $^1S^e$ and 1snd $^1D^e$ states will be followed by cascade fluorescence through 1smp $^1P^e$ ($m < n$) states into either the $1s^2$ $^1S^e$ or 1s2s $^1S^e$.

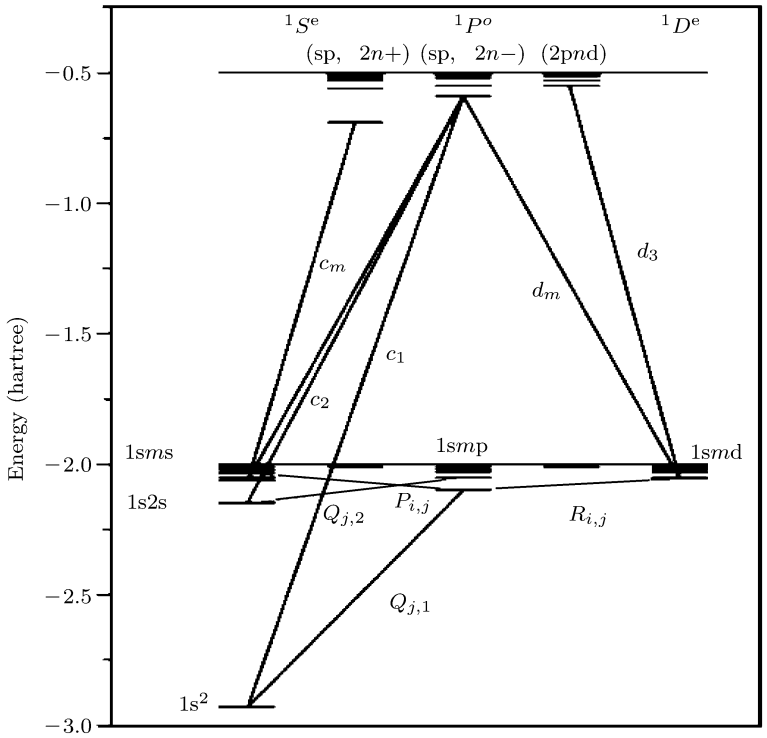


Fig.2. Schematic diagram of radiative decay scheme. Transitions shown with wider solid lines produce VUV photons. Other possible transitions are shown in thin lines.

Therefore, summing over one-step and cascade processes, and neglecting the VUV processes higher than one-step, whose contribution is very weak, the VUV photon yield intensity F_n and the metastable atom yield M_n, from a given doubly excited state n, can be described by the following formulas:[11]

$$F_n = \frac{f_n}{\Gamma_n}\left[\sum_i (c_i + d_{i+2}) + \sum_{i>2,j} c_i P_{ij} Q_{j1} + \sum_{ij} d_i R_{ij} Q_{j1}\right], \tag{13}$$

$$M_n = \frac{f_n}{\Gamma_n}\left[c_2 + \sum_{i>2,j} c_i P_{ij} Q_{j2} + \sum_{i,j} d_i R_{ij} Q_{j2}\right], \tag{14}$$

where c_i and d_i are the radiative decay rates to the 1sis $^1S^e$ and 1sid $^1D^e$ states, respectively, f_n is the oscillator strength from the ground state to the doubly excited state n, and

$$\Gamma_n = \Gamma_\alpha + \Gamma_{r,s} + \Gamma_{r,d} \tag{15}$$

is the total decay rate, where Γ_α is the Auger decay rate,

$$\Gamma_{r,s} = \sum_i c_i \tag{16}$$

and

$$\Gamma_{r,d} = \sum_i d_i \tag{17}$$

are the radiative decay rates from the doubly excited state n to $^1S^e$ and $^1D^e$ singly excited states respectively. $P_{i,j}$ and $R_{i,j}$ are the fluorescence branching ratios corresponding to 1sis→1sjp and 1sid→1sjp transitions, respectively, and $Q_{i,j}$ is the fluorescence branching ratio from 1sip to 1sjs. Our results are shown in Table 3 and Table 4, and are summarized in Table 5.

Table 3. Radiative decay rates c_i and d_i of doubly excited states corresponding, respectively, to transitions into 1sis $^1S^e$ and 1sid $^1D^e$ singly excited states. All decay rates are in units of s^{-1}.

State	$c1$	$c2$	$c3$	$c4$	$c5$	$d3$	$d4$
22+	3.5E+08	6.4E+09	2.1E+08	5.1E+07	1.9E+07	9.5E+07	3.5E+07
23+	7.7E+07	4.0E+07	5.7E+09	4.4E+07	1.5E+07	8.1E+08	4.4E+06
24+	2.9E+07	5.4E+05	1.8E+07	5.9E+09	1.9E+06	3.0E+05	6.0E+06
25+	1.5E+07	6.3E+06	5.9E+05	2.4E+07	5.7E+09	4.8E+05	2.2E+05
23-	2.2E+06	2.7E+09	1.5E+09	1.6E+08	5.1E+07	1.9E+08	1.8E+07
24-	7.7E+05	4.9E+08	1.2E+09	1.4E+09	1.9E+08	1.7E+07	1.3E+08
25-	6.4E+05	1.4E+08	9.9E+07	6.4E+07	3.1E+08	1.3E+07	2.9E+08
2p3d	1.4E+06	1.1E+07	6.2E+08	1.3E+08	1.2E+07	4.4E+09	3.5E+08
2p4d	4.2E+05	6.9E+07	1.3E+08	1.6E+09	2.2E+09	1.1E+08	1.5E+09

As seen from Table 3 (around the main diagonal), radiative decay proceeds preferentially form each doubly excited state n to 1sms or 1smd with $n \approx m$. As proposed by Odling-Smee *et al*,[8] for the contribution to the VUV photon yield, the radiative decay of 2p3d into 1s3d ($4.4 \times 10^9\,s^{-1}$) and 2p4d into1s4d ($1.5 \times 10^9\,s^{-1}$) is indeed significant and stronger than the autoionization at rates of ($6.2 \times 10^8\,s^{-1}$ and $1.2 \times 10^8\,s^{-1}$) respectively,[11] contrary to the decay rates of $2n^{\pm}$ states, which are dominated by autoionization.[11]

Table 4. A comparison of radiative decay rates (in s^{-1}) from the doubly excited $^1P^o$ sequence into singly excited state 1s2s $^1S^e$.

State	present work	Dickinson's[21]
22+	6.4E+09	6.6E+09
23+	4.0E+07	5.6E+07
24+	5.4E+05	1.7E+06
25+	6.4E+06	1.1E+07
23-	2.7E+09	2.8E+09
24-	4.9E+08	4.1E+08
25-	1.4E+08	1.1E+08
2p3d	1.1E+07	5.6E+07
2p4d	6.9E+07	4.2E+07

Table 5. Total (Γ) and total radiative decay rates (Γ_r), compared with these in Ref.[10], and the cascade rates of Eqs.13 and 14, corresponding, respectively, to transitions into 1sis $^1S^e$ (c(F_n), $c(M_n)$) and 1sid $^1D^e$ ($d(F_n)$, $d(M_n)$) (in s^{-1}), (5.7^{13} means 5.7×10^{13}).

State	Γ	Γ_r	Γ_r[10]	$c(F)$	$d(F)$	$c(M)$	$d(M)$
(sp,22^+)	5.7^{13}	7.2^9	6.94^9	2.8^8	1.3^8	2.1^8	5.1^7
(sp,23^+)	1.2^{13}	6.7^9	7.22^9	5.8^9	8.1^8	5.7^9	4.4^7
(sp,24^+)	5.3^{12}	6.0^9	7.52^9	5.9^9	6.3^6	1.8^7	5.9^9
(sp,25^+)	2.6^{12}	5.8^9	7.67^9	5.6^9	7.1^5	5.9^5	2.4^7
(sp,23^-)	1.7^{11}	4.6^9	5.33^9	1.7^9	2.1^8	1.5^9	1.6^8
(sp,24^-)	8.8^{10}	3.5^9	7.37^9	2.8^9	1.5^8	1.2^9	1.4^9
(sp,25^-)	4.2^{10}	9.2^8	7.88^9	4.6^8	3.0^8	9.9^7	6.4^7
(2p,3d)	6.2^9	5.6^9	4.22^9	7.7^8	4.8^9	6.2^8	1.3^8
(2p,4d)	5.8^9	5.7^9	3.77^9	3.9^9	1.6^9	1.3^8	1.6^9

We consider the oscillator strengths given by Liu *et al*,[10] as well as the branching ratios for singly excited states presented by Theodosiou[34] to be very accurate, because the orbital overlap between the ground state $1s^2$ (RMS spatial extent ≈1 a.u.) and the excited states (relevant orbital RMS spatial extent

being larger than 15 a.u.) is insignificant. Therefore we calculate the metastable atom (M_n) and the VUV photon yields (F_n) (see Fig.3) by using our radiative rates c_i and d_i from Table 3; the Auger rates, oscillator strengths, and branching ratios were cited from Chen,[25] Liu *et al*[10] and Theodosiou[34] respectively.

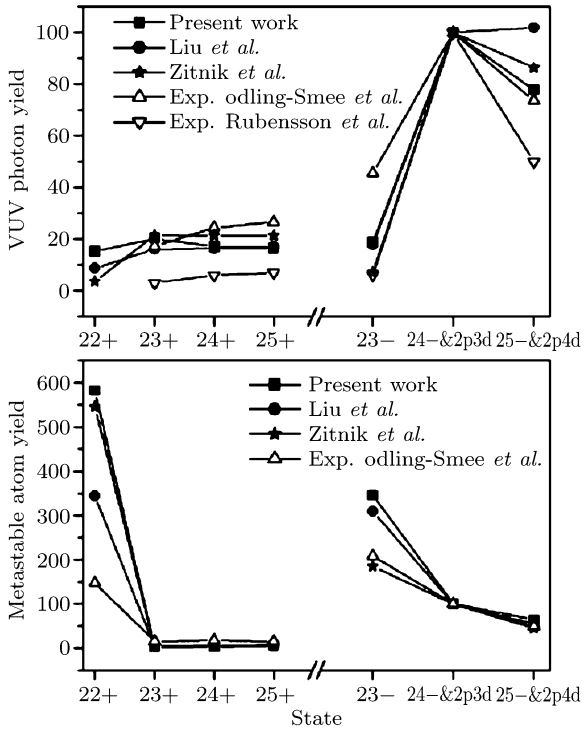


Fig.3. Relative peak intensities of metastable He atom and VUV photon yields, VUV photon yields normalized to the sum of He 24^- and 2p3d, and compared with the experimental results of Odling-Smee *et al*[8] and Rubensson *et al*[9] (obtained by adding the abscissas of the corresponding filled circles in Fig.3 of Ref.[9]) and with the calculations of Liu *et al.*[10] and Zitnik *et al*[11] (obtained by adding the abscissae of the corresponding columns in Fig.4 of Ref.[11]).

5. Results and discussion

In Fig.3, we show a comparison of our metastable atom and VUV photon yields with the experimental[8,9] and the theoretical ones.[10,11] In the experimental metastable atom spectrum, the intensities of $2n^{-1}P^{\rm o}$ states decrease as n increases. In the VUV photon spectrum, there appears an enhanced yield at the energy of 24^-/2p3d $^1P^{\rm o}$ state in both experiments. Actually, as Penent *et al*[12] clearly mentioned (in the 2nd paragraph, p.2759), five experimental results[8,9,11−13] agree with the comparable intensities—at least in a common energy region 64–65 eV. Our results qualitatively agree with these experimental results. Liu *et al*[10] have obtained good qualitative agreement with experimental results on metastable atom yields while their VUV photon yields show poor agreement (they did not predict the above enhancement).[10] Their calculations, using large B spline basis sets, are very accurate; however, it is not evident whether they considered non-orthogonality for the radiative transition between the doubly and the singly excited states if the orbitals appreciably overlap. Our wavefunctions compare well with those in the literature[21−23] as seen from Tables (1 and 2). In addition, our radiative decay rates (c_2) are compared reasonably with the only ones available in the literature[21] (see Table 5); our calculated lifetime of 161ps for the 2p3d state is more reasonable than 207 ps of Liu *et al*[10] because it is in accordance with the experimentally[35] determined upper limit for the lifetime of 190 ± 30 ps ($3.5 \pm 0.6\,\mu$eV in width). Therefore, we consider that our analytic calculations, due to nearly NMCSCF quality, are trustable. Therefore, we regard the experimental results, within an experimental error, as consistent, as predicted by Zitnik *et al.*[11] We attribute our results in fairly good agreement with the experimental ones to the inevitable non-orthogonality formalism, necessary for the main effect between the orbitals under consideration; The electrons spend some time in the excited state before they cascade to lower states. When they change their states, both the initial and the final orbitals instantaneously accommodate the same electron, so these two orbitals overlap each other, since, by the very physical understanding of the process, at places where the initial orbital had a maximum electron probability, the final orbital (although it may not be maximum there), certainly is not zero. Thus, the initial and final orbitals are not orthogonal, since orthogonality of two orbitals means that the second orbital has nodes in places where the first one is maximum. Therefore, the employed non-orthogonal formalism is essential.

6. conclusion

In conclusion, by presenting a general non-orthogonal calculation scheme for dipole matrix elements in the LS coupling, we calculate the radiative decay of low-lying doubly excited $^1P^{\rm o}$ states of He below the $\mathrm{He}^+(N = 2)$ ionization threshold. From

these rates, we calculate the VUV photon emission and metastable atom spectra. The good qualitative agreement of our calculations with the recent experimental results[8,9,11−13] on both metastable atom and VUV photon yields, strongly supports the proposition presented by Odling-Smee *et al*[8] that the radiative decay of the energetically narrow 2pnd states, preferentially to 1smd ($n \approx m$), is the key to understanding the observed VUV spectra. It also suggests that taking account of the non-orthogonality between the orbitals of doubly and singly excited states is essential in calculating these radiative transitions.

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References

[1] Madden R P and Codling K 1963 *Phys. Rev. Lett.* **10** 516
[2] Domke M, Schulz K, Remmers G, Kaindl G and Wintgenet D 1996 *Phys. Rev.* A **53** 1424 and references therein
[3] Cooper J W, Fano U and Prats F 1963 *Phys. Rev. Lett.* **10** 518
[4] Lin C D 1984 *Phys. Rev.* A **29** 1019
[5] Feagin J M and Briggs J S 1986 *Phys. Rev. Lett.* **57** 984
[6] Feagin J M and Briggs J S 1988 *Phys. Rev.* A **37** 4599
[7] Sadeghpour H R and Greene C H 1990 *Phys. Rev. Lett.* **65** 313
[8] Odling-Smee M K, Skoell E, Hammond P and MacDonald M A 2000 *Phys. Rev. Lett.* **84** 2598
[9] Rubensson J E, Såthe C, Cramm S, Kessler B, Stranges S, Richter R, Alagia M and Coreno M 1999 *Phys. Rev. Lett.* **83** 947
[10] Liu C N, Chen M K and Lin C D 2001 *Phys. Rev.* A **64** 010501(R)
[11] Zitnik M, Bucar K, Stuhec M, Penent F, Hall R I and Lablanquie P 2002 *Phys. Rev.* A **65** 032520
[12] Penent F, Lablanquie P, Hall R I, Zitnik M, Bucar K, Strangers S, Richter R, Alagia M, Hammond P and Lambourne J G 2001 *Phys. Rev. Lett.* **86** 2758
[13] Schartner K H, Zimmermann B, Kammer S, Mickat S, Schmoranzer H, Ehresmann A, Liebel H, Follath R and Reichardt G 2001 *Phys. Rev.* A **64** 040501(R)
[14] Xiong Zhuang and Bacalis N C 2006 *Chin. Phys.* **15** 992
[15] Xiong Z, Velgakis M J and Bacalis N C 2005 *Int. J. Quantum Chem.* **104** 418
[16] Friedrich H 1990 *Theoretical Atomic Physics* (New York: Springer-Verlag) p.108
[17] Sobelman I I 1977 *Atomic Spectra and Radiative Transitions* (New York: Springer) p.211
[18] McWeeny R 1989 *Methods of Molecular Quantum Mechanics* 2nd ed. (San Diego: Academic) p.66
[19] Fischer C F, Brage T and Jonsson P 1997 *Computational Atomic Structure, An MCHF Approach* (Bristol and Philadelphia: Institute of Physics Publishing) p.189
[20] Eckart C E 1930 *Phys. Rev.* **36** 878
[21] Dickinson H O and Rudge R H 1970 *J. Phys.* B **3** 1284
[22] Burke P G and McVicar D D 1965 *Proc. Phys. Soc.* **86** 989
[23] Lipsky L and Russek A 1966 *Phys. Rev.* **142** 59
[24] Hylleraas E and Undheim B 1930 *Z. Phys.* **65** 759
[25] Chen M K 1997 *Phys. Rev.* A **56** 4537
[26] Oza D H 1986 *Phys. Rev.* A **33** 824
[27] Ho Y K 1991 *Z. Phys.* D **21** 191
[28] Ho Y K 1993 *Phys. Rev.* A **48** 3598
[29] Wintgen D and Delande D 1993 *J. Phys.* B **26** L339
[30] Wu L and Xi J 1990 *J. Phys.* B **23** 727
[31] Venuti M, Decleva P and Lisini A 1996 *J. Phys.* B **29** 5315
[32] Chen M K 1993 *J. Phys.* B **26** 3025
[33] Chen M K 1994 *J. Phys.* B **27** 4847
[34] Theodosiou C E 1987 *At. Date Nucl. Data Tables* **36** 97
[35] Lambourne J G, Penent F, Lablanquie P, Hall R I, Ahmad M, Zitnik M, Bucar K, Odling-Smee M K, Harries J R, Hammond P, Waterhouse D K, Stranges S, Richter R, Alagia M, Coreno M and Ferianis M 2003 *Phys. Rev. Lett.* **90** 153004