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Fluorescence yield for the beryllium atom*

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The fluorescence yield for a beryllium atom in the vacancy state $1s(2s)^2\,{}^2S$ is calculated. The radiative decay rate is shown to arise from correlation effects. The fluorescence yields for the $1s2s2p\,{}^2P$ vacancy states are also calculated and found to be very large.

Fluorescence yields have been of considerable interest in physics for many years, and two excellent reviews of this subject have recently been published.[1,2] The fluorescent yield ω_i for a given inner-shell vacancy i is defined by[2]

$$\omega_i = P_R^i/(P_R^i + P_A^i), \tag{1}$$

where P_R^i is the sum of the transition rates for all radiative transitions to fill the vacancy i, and P_A^i is the sum of all Auger rates to fill the vacancy.

The K-shell fluorescence yields have been measured and calculated for almost all atoms.[1] A notable exception is beryllium, for which there are two experimental values[3,4] but no calculations. At first, this seems quite surprising since beryllium is the smallest atom for which one can have a nonzero Auger rate when there is a simple $1s$ hole. However, almost all calculations[5-7] thus far have used an independent-particle model with orbitals calculated in a Hartree-States potential or a potential of lesser accuracy.

If we attempt to calculate the radiative decay rate for a Be^+ atom in the $1s(2s)^2$ configuration, the radiative decay rate via electric dipole transitions is zero to the $1s^22s$ state. However, when electron correlations are included, there is a nonzero electric dipole transition rate to the $(1s)^2np\,{}^2P$ states. For example, the $1s(2s)^2\,{}^2S$ state is expected to have a significant admixture of $1s(2p)^2\,{}^2S$, and the $1s(2p)^2\,{}^2S$ state can make a dipole transition to $1s^22p\,{}^2P$.

Although it is expected that the admixture of $1s(2p)^2\,{}^2S$ into $1s(2s)^2\,{}^2S$ causes the most important effect in this case, we also consider all processes which are first order in the Coulomb interaction and also in the dipole matrix element, and lead to the $1s^2np\,{}^2P$ final states. The various contributions to $\langle\Psi_f|\Sigma\,\vec{r}_i\,|\Psi_i\rangle$, where $|\Psi_i\rangle$ and $|\Psi_f\rangle$ are the correlated many-electron states $1s(2s)^2\,{}^2S$ and $1s^2np\,{}^2P$, respectively, are shown in Fig. 1. We have used the diagrammatic notation of many-body perturbation theory.[8,9] The dashed line between two solid lines represents the Coulomb interaction, and the heavy dot corresponds to interaction with the radiation field. For example, in Fig. 1(a) the bottom interaction corresponds to the matrix element $\langle 1sks|v|2s2s\rangle$, where $v=|\vec{r}_i - \vec{r}_j|^{-1}$. The top interaction in Fig. 1(a) (using the dipole approximation) corresponds to the matrix element $\langle np|\vec{r}|ks\rangle$. In diagrams 1(a)–1(d) the intermediate states labeled ks or kp refer, of course, to sums over all bound and continuum excited states with $l=0$ or 1, respectively. In the diagrams, the time ordering is from bottom to top, corresponding to interactions from right to left in the matrix element $\langle\Psi_f|\Sigma\,\vec{r}_i|\Psi_i\rangle$. Coulomb interactions ocurring before (after) the dipole interaction correspond to correlations in $|\Psi_i\rangle(|\Psi_f\rangle)$. Diagrams (a) and (b) represent admixtures of $1s^2ks\,{}^2S$ and $1skpnp\,{}^2S$ into $1s(2s)^2\,{}^2S$. Diagrams (c) + (d), (e), and (f) represent admixtures of $1s2skp\,{}^2P$, $(2s)^2np\,{}^2P$, and $1s2snp\,{}^2P$ into $(1s)^2np\,{}^2P$. Higher-order diagrams which were expected to be important and were explicitly calculated are shown in Fig. 2.

Hartree-Fock calculations were carried out to obtain the single-particle states which were needed to evaluate the various terms of Figs. 1 and 2. The diagrams were calculated as discussed previously[10] except for the $(2s)^2 \to (2p)^2$ excitations. Since the $(2s)^2 \to (2p)^2$ excitations are expected to give the largest contributions, the admixture of $(2p)^2\,{}^1S$ into $(2s)^2\,{}^1S$ was determined by means of a multiconfiguration Hartree-Fock calculation. The result of this calculation for Ψ_i was found to be

$$\Psi_i = (0.940\,88)1s2s^2\,{}^2S + (0.338\,73)1s2p^2\,{}^2S. \tag{2}$$

The remaining $l=1$ states were approximately orthogonalized to the $2p$ state. Atomic units are used throughout this paper.

Contributions of the diagrams of Figs. 1 and 2 to the quantity $\langle\Psi_f|\Sigma_{i=1}^3 r_i|\Psi_i\rangle$, with $|\Psi_f\rangle$ equal to $1s^22p\,{}^2P$, are given in Table I. Note that the angular factor for the dipole interaction is not included so that $\langle\Psi_f|\Sigma_i z_i|\Psi_i\rangle$, for example, is given by $3^{-1/2}$ times the values listed. The largest contribution in Table I comes from the diagram of Fig. 1(b). This value is almost entirely due to the $(2s)^2 \rightarrow (2p)^2$ excitation. In Fig. 1(b), excitations into continuum states contribute 0.002 333 and excitations into bound excited states with $n \geqslant 3$ contributed −0.003 142.

The radiative decay rate[11]

$$P_R = \tfrac{4}{3}\alpha \frac{\omega^3}{c^2}\left| \langle \Psi_f | \sum_{i=1}^{3} \vec{\mathrm{r}}_i | \Psi_i \rangle \right|^2 , \tag{3}$$

where α is the fine-structure constant. The quantity ω is the energy of the emitted photon and is equal to the energy of $1s2s^2\,{}^2S$ minus the energy of $1s^22p\,{}^2P$. The Hartree-Fock energy of $1s^22p$ was calculated to be −14.130 86 a.u. The correlation energy of $1s^2$ was taken from previous calculations[12] of neutral beryllium to be −0.042 12 a.u. The energy for the $1s(2s)^2$ state was calculated by the multiconfiguration program to be −10.102 661 a.u. The resulting value for ω is 4.070 319 a.u. Using this result for ω and the result of Table I, P_R for the final state $(1s)^2\,2p$ is 7.338×10^{-8} a.u.

The transition rate to the final state $1s^23p\,{}^2P$ was also calculated and was found to be 0.305×10^{-8} a.u. Our calculated values for the energy of the photons emitted in these transitions to the $(1s)^22p$ and $(1s)^23p$ states are 4.0703 and 3.7792 a.u., respectively.

In order to obtain the fluorescence yield, it is necessary to calculate also the Auger rate. Using our standard normalization for continuum states,[10]

$$P_{kl}(r) = \cos[kr + \delta_l + (q/k)\ln 2kr - (l+1)\pi/2], \tag{4}$$

as $r \rightarrow \infty$, the Auger rate is then[13]

$$P_A = \frac{4}{k_0}\left| \langle \Psi_f | \sum_{i<j} v_{ij} | \Psi_i \rangle \right|^2 , \tag{5}$$

where

$$k_0 = [2(E_i - E_f)]^{1/2} . \tag{6}$$

For the state Ψ_i, the configuration-mixed state of Eq. (2) was used. The final state Ψ_f is the Hartree-Fock state $1s^2ks$. The matrix element of Eq. (5) was calculated to be 0.047 699 a.u., with 0.040 808 a.u. from the $1s2s^2$ configuration and 0.006 891 a.u. from the $1s(2p)^2$ configuration. The Auger rate P_A is then 3.4151×10^{-3} a.u.

When configuration mixing is not considered, the Auger rate is 1.81×10^{-3} a.u., the bound states being calculated with the restricted Hartree-Fock program of Froese Fischer.[14] It is found then that the configuration mixing approximately doubles the rate. We note that our KL_1L_1 Auger rate for Be is larger than the value 0.82×10^{-3} a.u. which we calculated previously for Ne.[13] There is a factor of 2 increase owing to configuration mixing of $(2s)^2$-$(2p)^2$ in the initial state which takes place for Be but cannot occur for Ne since the $2p$ shell is closed. In addition, the restricted

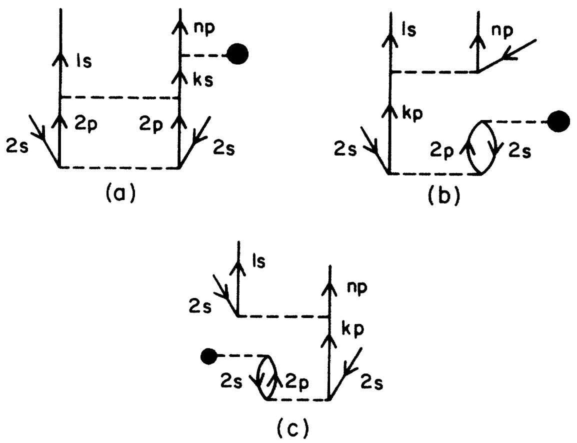

FIG. 1. Lowest-order diagrams contributing to the matrix element $\langle \Psi_f | \sum_i \vec{r}_i | \Psi_i \rangle$, with $| \Psi_i \rangle$ equal to $1s(2s)^2\,{}^2S$ and $| \Psi_f \rangle$ equal to $(1s)^2np\,{}^2P$. The heavy dot corresponds to interaction with $\vec{r}$. The dashed line between two solid lines corresponds to Coulomb interaction.

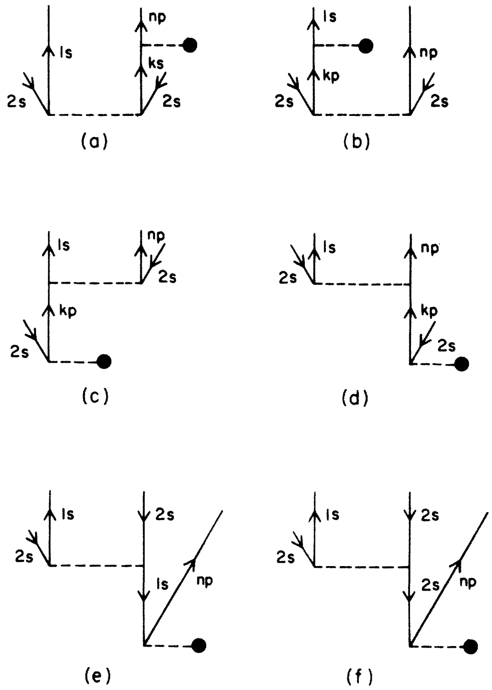

FIG. 2. Selected second-order (in the Coulomb interactions) diagrams which are expected to be most important for $\langle \Psi_f | \sum \vec{r}_i | \Psi_i \rangle$, with $| \Psi_i \rangle$ equal to $1s(2s)^2\,{}^2S$ and $| \Psi_f \rangle$ equal to $(1s)^2np\,{}^2P$. The heavy dot corresponds to interaction with $\vec{r}$.

Hartree-Fock value for Be is larger (by approximately a factor of 2) than for Ne. We attribute this to the increased importance of exchange terms for low Z in calculating the single-particle states. There is a general increase in the KL_1L_1 rate calculated in the restricted Hartree-Fock approximation as one goes from Ne to Be,[15] as compared with a KL_1L_1 rate which is independent of Z when hydrogenic states are used.[2] We note that the Hartree-Fock-Slater (HFS) calculations of Walters and Bhalla[16] indicate KL_1L_1 rates approximately constant from Ne to Be. The approximate HFS calculations of McGuire[7] indicate approximately constant KL_1L_1 rates from C to Ne, with deviations at Be and B.

Considering radiative transitions to $(1s)^2 2p\ {}^2P$, the fluorescence yield is then 0.2149×10^{-4}. This value is increased somewhat by considering transitions to all final states $(1s)^2 np$ including the continuum. However, it is estimated that this sum will not cause a large increase in the fluorescence yield. The contribution from $(1s)^2 3p$ is much smaller than that from $(1s)^2 2p$.

There is, however, another consideration which might have a very large effect on any measured fluorescence yields for the beryllium atom. This is the possibility that the photoionization does not merely remove a $1s$ electron but also simultaneously excites an outer electron. Such processes have been considered recently both experimentally[17,18] and theoretically[16] for helium and were found to be significant. For example, at photon energies of 100 eV, the ratio of the cross section[19] for leaving He^+ in the $n = 2$ level to that for He^+ with $n = 1$ is approximately 0.10, with a significant number of $n = 2$ electrons having $l = 1$.

If the photoionization of Be resulted in excited states $(1s(2s2p)\,{}^1P)\,{}^2P$ and $(1s(2s2p)\,{}^3P)\,{}^2P$ even a small fraction of the time, it could have a significant effect upon the fluorescent yield because we expect much larger radiative rates in these cases than for the $1s(2s)^2$ initial state.

The Hartree-Fock approximation was used to calculate the radiative and Auger decay rates for these $1s2s2p\ {}^2P$ states. These results are listed in Table II along with the rates arising from the $1s(2s)^2$ initial state.

The energies of the photons emitted in the radiative decays of the $(1s(2s2p)\,{}^3P)\,{}^2P$ and $(1s(2s2p)\,{}^1P)\,{}^2P$ states are calculated to be 4.363 and 4.452 a.u., respectively. Correlation effects were not included.

The fluorescence yields for the $(1s(2s2p)\,{}^3P)\,{}^2P$ and $(1s(2s2p)\,{}^1P)\,{}^2P$ states are calculated to be 54.36×10^{-4} and 44.69×10^{-4}, respectively. This is to be compared with a fluorescence yield from $1s(2s)^2\ {}^2S$ of 0.2238×10^{-4} when radiative transitions to both $(1s)^2 2p$ and $(1s)^2 3p$ final states are included. It is estimated that the remaining $(1s)^2 np$ and $(1s)^2 kp$ excitations will not increase this value appreciably. If even a small fraction of the photoionized atoms are in $1s2s2p\ {}^2P$ states it can clearly change the observed fluorescence yield drastically. For example, consider a distribution of photoionized Be^+ atoms with 95, 3, and 2% in the states $1s(2s)^2\ {}^2S$, $(1s(2s2p)\,{}^3P)\,{}^2P$, and $(1s(2s2p)\,{}^1P)\,{}^2P$, respectively. The observed fluorescent yield would be 2.737×10^{-4}. Therefore, it is expected that any experiment on Be may well give a fluorescence yield very different from that of a pure $1s(2s)^2\ {}^2S$ vacancy.

The $1s(2s)^2\ {}^2S$ state can decay by magnetic dipole radiation or by two-photon decays; but these are estimated on the basis of previous work[20] on H and He to be much smaller than the electric dipole transition due to correlations.

Fluorescence-yield experiments on Be, B, C, F, and Mg have been reported by Dick and Lucas[3] and on Be, B, and C by Feser.[4] The Be fluorescence yields are $3.04 \times 10^{-4} \pm 20\%$ obtained by Dick

TABLE I. Contributions to $\langle 1s^2 2p\ {}^2P \,|\, \Sigma r_i \,|\, 1s(2s)^2\ {}^2S \rangle$ from the diagrams of Figs. 1 and 2. (Angular factor for the dipole interaction is not included.)

Diagram	Value (a.u.)
1(a)	0.008 957
1(b)	−0.054 067
1(c)	−0.004 646
1(d)	−0.004 162
1(e)	0.002 430
1(f)	0.000 629
2(a)	0.003 307
2(b)	0.000 909
2(c)	0.000 814
Total	−0.045 829

TABLE II. Radiative and Auger decay rates for Be

Initial state	Decay type	Final state[a]	Rate (a.u.)[b]
$1s(2s)^2\ {}^2S$	Radiative	$(1s)^2 2p\ {}^2P$	7.338(−8)[c]
$1s(2s)^2\ {}^2S$	Radiative	$(1s)^2 3p\ {}^2P$	0.305(−8)[d]
$1s(2s)^2\ {}^2S$	Auger	$(1s)^2 ks\ {}^2S$	3.415(−3)
$(1s(2s2p)\,{}^3P)\,{}^2P$	Radiative	$(1s)^2 2s\ {}^2S$	4.980(−6)[e]
$(1s(2s2p)\,{}^3P)\,{}^2P$	Auger	$(1s)^2 kp\ {}^2P$	9.111(−4)
$(1s(2s2p)\,{}^1P)\,{}^2P$	Radiative	$(1s)^2 2s\ {}^2S$	1.998(−6)[f]
$(1s(2s2p)\,{}^1P)\,{}^2P$	Auger	$(1s)^2 kp\ {}^2P$	4.450(−4)

[a] k refers to an electron in the continuum.

[b] Value in parentheses indicates multiplication by powers of ten.

[c] Emitted photon energy 4.0703 a.u.

[d] Emitted photon energy 3.7792 a.u.

[e] Emitted photon energy 4.363 a.u.

[f] Emitted photon energy 4.452 a.u.

and Lucas[3] and $3.6\times10^{-4}\pm30\%$ obtained by Feser.[4] Since solid beryllium targets were used in both experiments,[3,4] it does not seem meaningful to compare the experimental results with atomic calculations. In the solid the $2s$ electrons are now in the valence band and possess some $l=1$ character. Therefore, radiative transitions to the $1s$ level are allowed even in the absence of correlations. It is not surprising that the fluorescence yield for solid Be is larger than that obtained for atomic Be with a vacancy state $1s(2s)^2\,{}^2S$.

The fluorescence yield for atomic Be is interesting because the radiative decay rate for the $1s(2s)^2\,{}^2S$ state would be zero except for correlation effects. However, it should be extremely difficult to prepare Be purely in the atomic vacancy state $(1s)(2s)^2\,{}^2S$. The fluorescence yield will be strongly affected by even small admixtures of $1s2s2p\,{}^2P$ states. The expected admixture of $1s2s2p\,{}^2P$ resulting from photoionization could be calculated as discussed previously[21] for Fe, and this will be investigated in a future paper.

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