TABLE I. Lifetime of Mg^+ $3^2P_{3/2}$ state.

Method	Reference	Result
SCF[a] with exchange and polarization approximations	33	3.84×10^{-9} sec
Coulomb approximation	34	3.97×10^{-9} sec
Arc emission	35	$4.4\ \times10^{-9}$ sec (std. dev. of $\log_{10}\tau=0.27$)
Hanle effect	present work	$(3.67\pm0.18)\times10^{-9}$ sec

[a] Self-consistent-field.

dipole) perturbation potential of atom-atom collisions. (**P** is the dipole operator for the atom, **Π** is the dipole operator for the ion, and **R** is the internuclear vector.) It can be seen that this additional term will not directly produce changes in the density matrix of an excited state of the ion. The added term does make a contribution ($\sim R^{-6}$) in second-order perturbation theory when it is multiplied by a matrix element involving the electron quadrupole operator for the ion and the electron dipole operator for the atom. Second order is also the lowest order in which the dipole-dipole perturbation contributes (again $\sim R^{-6}$). One can verify that the added term involves matrix elements and energy denominators of the same order of magnitude as the dipole-dipole term. For this reason it is not surprising that the Group II ion-argon and atom-argon depolarization cross sections are of the same order of magnitude; they are also comparable to the theoretical and experimental cross sections for argon collisions with Hg in the lowest $^3P_1$ state quoted in Table II of Ref. 26.

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Calculation of Auto-Ionization Rates*

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A method has been formulated to calculate auto-ionization rates by perturbation theory with no internal inconsistencies. Calculations have been carried out in $(2s)^2\ ^1S$ He, $(2s,2p)\ ^{1,3}P$ He, $(1s,2s,2p)\ ^4P_{5/2}$ Li, and $(1s,2s,2p)\ ^2P_\pm$ Li. The applicability of this formulation, as well as how it differs from previous perturbation methods, is discussed.

I. INTRODUCTION

AN atom in an excited state lying above the first ionization potential may undergo a radiationless decay into the continuum. This is the phenomenon of auto-ionization. It is of significance in the interpretation of atomic spectra as well as being one of the more important processes in the upper atmosphere.

Many attempts[1–6] have been made to calculate the decay rate of auto-ionizing states. We shall be concerned with the perturbation-theory approach in this paper. A formulation is here presented which removes the internal inconsistencies that occurred in previous perturbation-theory calculations and is then used to calculate auto-ionization decay rate in certain states of helium and lithium.

Throughout this paper atomic units are used unless otherwise specified, i.e., $\hbar=e=m_{\text{electron}}=1$.

II. THE GOLDEN RULE

Suppose we have an atom with Hamiltonian H, and that at $t=0$ the atom is known to be in a state $|\varphi\rangle$. Let H_0 be a Hamiltonian such that

$$H_0|\varphi\rangle=E_0|\varphi\rangle, \tag{1}$$

where E_0 is the energy of the state. In the Schrödinger representation, then, $|\psi_s(t=0)\rangle=|\varphi\rangle$. Now we transform to the interaction representation defined by H_0; $|\psi_{\text{int}}(t=0)\rangle=|\varphi\rangle$. Define

$$H_1=H=H_0. \tag{2}$$

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Then, in this representation, the time-development operator, $U(t,0)$, is to second order:

$$U(t,0)=1-i\int_0^t e^{iH_0\tau}H_1e^{-iH_0\tau}d\tau-\int_0^t\int_0^\tau e^{iH_0\tau}\times e^{-iH_0\tau}e^{iH_0\tau'}H_1e^{-iH_0\tau'}d\tau'd\tau\,, \quad (3)$$

$$|\psi_{\text{int}}(t)\rangle=U(t,0)|\psi_{\text{int}}(t=0)\rangle=U(t,0)|\varphi\rangle. \quad (4)$$

The probability, then, that the atom will remain in its initial state after time t is

$$P=|\langle\psi_{\text{int}}(t=0)|\psi_{\text{int}}(t)\rangle|^2. \quad (5)$$

Thus

$$P=|\langle\varphi|U(t,0)|\varphi\rangle|^2=\left|1-i\int_0^t\langle\varphi|e^{iE_0\tau}H_1e^{-iE_0\tau}|\varphi\rangle d\tau-\int_0^t\int_0^\tau\langle\varphi|e^{iE_0\tau}H_1e^{-iH_0\tau}e^{iH_0\tau'}H_1e^{-iE_0\tau'}|\varphi\rangle d\tau'd\tau\right|^2. \quad (6)$$

Introducing a unit operator $I=\sum_f|\varphi_f\rangle\langle\varphi_f|$, where the $|\varphi_f\rangle$ form a complete orthonormal set and $\sum_f$ means sum over discrete, integrate over continuum states with density of states factor,

$$P=\left|1-it\langle\varphi|H_1|\varphi\rangle-\sum_f\int_0^t\int_0^\tau\langle\varphi|e^{iE_0\tau}H_1e^{-iH_0\tau}|\varphi_f\rangle\times\langle\varphi_f|e^{iH_0\tau'}H_1e^{-iE_0\tau}|\varphi\rangle d\tau'd\tau\right|^2. \quad (7)$$

Let the $|\varphi_f\rangle$ be the solutions to H_0. Then

$$P=\left|1-it\langle\varphi|H_1|\varphi\rangle-\sum_f|\langle\varphi|H_1|\varphi_f\rangle|^2\times\int_0^t\int_0^\tau e^{i(E_f-E_0)(\tau'-\tau)}d\tau'd\tau\right|^2. \quad (8)$$

Thus, setting $\omega=E_f-E_0$ and integrating,

$$P=\left|\left[1-\sum_f|\langle\varphi|H_1|\varphi_f\rangle|^2\frac{(1-\cos\omega t)}{\omega^2}\right]+i\left[-t\langle\varphi|H_1|\varphi\rangle+\sum_f|\langle\varphi|H_1|\varphi_\sigma\rangle|^2\times\left(-\frac{t}{\omega}+\frac{\sin\omega t}{\omega^2}\right)\right]\right|^2. \quad (9)$$

Hence, keeping terms up to second order,

$$P=1-\sum_f|\langle\varphi|H_1|\varphi_f\rangle|^2\frac{2(1-\cos\omega t)}{\omega^2}-t^2\langle\varphi|H_1|\varphi\rangle^2$$

$$=1-\sum_{f,\varphi_f\neq\varphi}|\langle\varphi|H_1|\varphi_f\rangle|^2\frac{2(1-\cos\omega t)}{\omega^2}. \quad (10)$$

The probability that the atom is not in the initial state after time t, W, is then

$$W=\sum_{f,\varphi_f\neq\varphi}|\langle\varphi|H_1|\varphi_f\rangle|^2\frac{2(1-\cos\omega t)}{\omega^2}. \quad (11)$$

The spectrum of states $|\varphi_f\rangle$ consists of a series of discrete states plus a continuum which is adjacent to some of the states; in particular, to $|\varphi\rangle$. Then if we assume that there are no discrete states so close to $|\varphi\rangle$ such that $\omega t\ll 1$ for t of the order of the decay time, the only significant contribution to W is from the continuum state where $\omega=0$, since $(1-\cos\omega t)/\omega^2$ is very sharply peaked about $\omega=0$. Thus

$$W=\int_{E_{\min}}^\infty|\langle\varphi|H_1|\varphi_f\rangle|^2\rho(E_f)\frac{2(1-\cos\omega t)}{\omega^2}dE_f$$

$$=|\langle\varphi|H_1|\varphi_f(E_f=E_0)\rangle|^2\rho(E_0)\int_{E_{\min}}^\infty\frac{2(1-\cos\omega t)}{\omega^2}dE_f$$

$$=|\langle\varphi|H_1|\psi\rangle|^2\rho(E_0)\int_{-\infty}^\infty\frac{2(1-\cos\omega t)}{\omega^2}d\omega$$

$$=2\pi|\langle\varphi|H_1|\psi\rangle|^2\rho(E_0)t\,, \quad (12)$$

where $\psi=\varphi_f(E_f=E_0)$. The decay rate, R, is then

$$R=2\pi|\langle\varphi|H_1|\psi\rangle|^2\rho(E_0)\,, \quad (13)$$

the Golden rule.

III. PREVIOUS PERTURBATION CALCULATIONS

In most earlier perturbation work[1–4] one started with a wave function $|\varphi_i\rangle$ representing the initial discrete state of the N-electron system which was obtained by a variation procedure. Next a $|\varphi_f\rangle$ to approximate the final continuum state was found. Then the rate was calculated as

$$R=2\pi\left|\langle\varphi_i|\sum_{i<j}^N\frac{1}{r_{ij}}|\varphi_f\rangle\right|^2\rho(E_i).$$

This procedure is usually inconsistent, since, as has been shown in the previous section, $|\varphi_i\rangle$ and $|\varphi_f\rangle$ must be solutions to the same H_0 which is not generally true here. Further, the perturbing potential, $H_1=H-H_0$, is not defined unless H_0 is, and it is not, in general, equal to $\sum_{i<j}^N(1/r_{ij})$.

To surmount these difficulties, Bransden and Dalgarno[5] found an H_0 of which $|\varphi_i\rangle$ was an eigenfunction at energy E. Then, in the case of the $(2s)^2\,{}^1S_0\to(1s)(ks)\,{}^1S_0$ transition in helium, they write the final state in the form

$$|\varphi_f\rangle=(1/\sqrt{2})[u(1)F(2)+u(2)F(1)],$$

where u is the wave function of the $(1s)$ state in He^+. F is then determined by the equation

$$\langle u(1)|H_0|\varphi_f\rangle=E\langle u(1)|\varphi_f\rangle \quad (14)$$

and the rate calculated as $R=2\pi|\langle\varphi_i|H-H_0|\varphi_f\rangle|\rho(E)$. The $|\varphi_f\rangle$ thus obtained, however, is not a solution to H_0 and it is not even orthogonal to $|\varphi_i\rangle$.

IV. AN IMPROVED FORMULATION

Consider a system of N electrons and a nucleus of charge Z. The total Hamiltonian of such a system, H, is

$$H=\sum_{i=1}^{N}\left(T_i-\frac{Z}{r_i}\right)+\sum_{i<j}^{N}\frac{1}{r_{ij}}+\frac{\alpha^2}{2}\left[Z\sum_{i=1}^{N}\frac{\mathbf{l}_i\cdot\mathbf{s}_i}{r_i^3}-\sum_{i\neq j}^{N}\left(\frac{\mathbf{r}_{ij}}{r_{ij}^3}\times\mathbf{P}_i\right)\cdot(\mathbf{s}_i+2\mathbf{s}_j)+\sum_{i\neq j}^{N}\frac{1}{r_{ij}^3}\left(\mathbf{s}_i\cdot\mathbf{s}_j-3\frac{(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right)\right],\quad(15)$$

where

$$T_i=-\frac{1}{2r_i}\frac{\partial^2}{\partial r_i^2}r_i+\frac{l_i(l_i+1)}{2r_i^2},$$

the kinetic energy. Suppose the atom is initially in an auto-ionizing state described by the Hartree-Fock wave function, $|\varphi_i\rangle$, which we assume to be a good approximation. Then we find a symmetric, Hermitian, separable H_0 to which $|\varphi_i\rangle$ is a solution at the Hartree-Fock energy E_0. H_0 is constructed so that it will have a continuum solution, $|\varphi_f\rangle$, at energy E_0. Then the rate $R=2\pi|\langle\varphi_i|H-H_0|\varphi_f\rangle|^2\rho(E_0)$ is computed.

To illustrate, consider first the $(2s,2p)\,{}^1P_1\to(1s,kp){}^1P_1$ transition in helium. The form of the initial state is

$$|\varphi_i\rangle=(1/\sqrt{2})[u_{2s}(1)Y_0^0(1)u_{2p}(2)Y_1^1(2)+u_{2s}(2)Y_0^0(2)u_{2p}(1)Y_1^1(2)](1/\sqrt{2})[\chi_{1/2}(1)\chi_{-1/2}(2)-\chi_{-1/2}(1)\chi_{1/2}(2)],\quad(16)$$

where $\chi_{\pm 1/2}$ are the Pauli spinors and u_{2s}, u_{2p} are determined by the Hartree-Fock equations

$$T_1u_{2s}(1)-\frac{2}{r_1}u_{2s}(1)+f(1)u_{2s}(1)+h(1)u_{2p}(1)=-\lambda_1u_{2s}(1),\quad(17a)$$

$$T_2u_{2p}(2)-\frac{2}{r_2}u_{2p}(2)+g(2)u_{2p}(2)+h(2)u_{2s}(2)=-\lambda_2u_{2p}(2),\quad(17b)$$

where

$$f(1)=\int\int u_{2p}(2)Y_1^{1*}(2)Y_0^0(1)\frac{1}{r_{12}}u_{2p}(2)Y_1^1(2)Y_0^0(1)d\mathbf{r}_2d\Omega_1,\quad(18a)$$

$$g(2)=\int\int u_{2s}(1)Y_0^0(1)Y_1^{1*}(2)\frac{1}{r_{12}}u_{2s}(1)Y_0^0(1)Y_1^1(2)d\mathbf{r}_1d\Omega_2,\quad(18b)$$

$$h(1)=\int\int u_{2p}(2)Y_1^{1*}(2)Y_0^0(1)\frac{1}{r_{12}}u_{2s}(2)Y_0^0(2)Y_1^1(1)d\mathbf{r}_2d\Omega_1=h(1)^*,\quad(18c)$$

where u_{2s}, u_{2p} are real. The Hartree-Fock energy is $E_0=-\lambda_1-\lambda_2-K$, where

$$K=\langle u_{2s}(1)Y_0^0(1)u_{2p}(2)Y_1^1(2)|1/r_{12}|u_{2s}(1)Y_0^0(1)u_{2p}(2)Y_1^1(2)+u_{2s}(2)Y_0^0(2)u_{2p}(1)Y_1^1(1)\rangle.\quad(19)$$

Then

$$H_0=T_1+T_2-2/r_1-2/r_2+Q(1)+Q(2)-K,\quad(20)$$

$$\begin{aligned}Q(1)=|Y_0^0(1)\rangle f(1)\langle Y_0^0(1)|+|Y_1^1(1)\rangle g(1)\langle Y_1^1(1)|&\\+h(1)|u_{2s}(1)Y_1^1(1)\rangle\langle u_{2p}(1)Y_1^1(1)|+|u_{2p}(1)Y_1^1(1)\rangle\langle u_{2s}(1)Y_1^1(1)|h(1)&\\+h(1)|u_{2p}(1)Y_0^0(1)\rangle\langle u_{2s}(1)Y_0^0(1)|+|u_{2s}(1)Y_0^0(1)\rangle\langle u_{2p}(1)Y_0^0(1)|h(1)&\\-|u_{2s}(1)Y_0^0(1)\rangle\langle u_{2p}(2)Y_1^1(2)|h(2)|u_{2s}(2)Y_1^1(2)\rangle\langle u_{2s}(1)Y_0^0(1)|&\\-|u_{2p}(1)Y_1^1(1)\rangle\langle u_{2s}(2)Y_0^0(2)|h(2)|u_{2p}(2)Y_0^0(2)\rangle\langle u_{2p}(1)Y_1^1(1)|.&\quad(21)\end{aligned}$$

Writing $H_0=h_0(1)+h_0(2)-K$, Eqs. (17) become

$$h_0(1)|u_{2s}(1)Y_0^0(1)\rangle=-\lambda_1|u_{2s}(1)Y_0^0(1)\rangle,\quad(22a)$$

$$h_0(2)|u_{2p}(2)Y_1^1(2)\rangle=-\lambda_2|u_{2p}(2)Y_1^1(2)\rangle.\quad(22b)$$

The form of $|\varphi_f\rangle$, the "final" state is

$$|\varphi_f\rangle=(1/\sqrt{2})[a_{1s}(1)Y_0^0(1)b_{kp}(2)Y_1^1(2)+a_{1s}(2)Y_0^0(2)b_{kp}(1)Y_1^1(1)](1/\sqrt{2})[\chi_{1/2}(1)\chi_{-1/2}(2)-\chi_{1/2}(2)\chi_{-1/2}(1)]. \tag{23}$$

Then, separating $H_0|\varphi_f\rangle=E_0|\varphi_f\rangle$, we have

$$h_0(1)|a_{1s}(1)Y_0^0(1)\rangle=-\epsilon|a_{1s}(1)Y_0^0(1)\rangle, \tag{24a}$$

$$h_0(2)|b_{kp}(2)Y_1^1(2)\rangle=(\epsilon-\lambda_1-\lambda_2)|b_{kp}(2)Y_1^1(2)\rangle. \tag{24b}$$

Hence, since $\epsilon\neq\lambda_1$, $\epsilon-\lambda_1-\lambda_2\neq-\lambda_2$, and $h_0(i)$ is a Hermitian operator,

$$\langle a_{1s}|u_{2s}\rangle=0, \quad \langle b_{kp}|u_{2p}\rangle=0. \tag{25}$$

Equations (24) then reduce to

$$T_1a_{1s}(1)-(2/r_1)a_{1s}(1)+f(1)a_{1s}(1)+\langle u_{2p}(2)Y_0^0(2)|h(2)|a_{1s}(2)Y_0^0(2)\rangle u_{2s}(1)=-\epsilon a_{1s}(1), \tag{26a}$$

$$T_2b_{kp}(2)-(2/r_2)b_{kp}(2)+g(2)b_{kp}(2)+\langle u_{2s}(1)Y_1^1(1)|h(1)|b_{kp}(1)Y_1^1(1)\rangle u_{2p}(2)=(\epsilon-\lambda_1-\lambda_2)b_{kp}(2). \tag{26b}$$

Thus

$$R=2\pi|\langle\varphi_i|H-H_0|\varphi_f\rangle|^2\rho(E_0). \tag{27}$$

Because of Eqs. (24) however, only the two-electron interactions in $H-H_0$ will give a nonvanishing contribution to the rate. Further, we can to an excellent approximation, neglect the fine structure part of H as small compared with $1/r_{12}$. Then,

$$\begin{aligned}R&=2\pi|\langle\varphi_i|1/r_{12}|\varphi_f\rangle|^2\rho(E_0)\\&=2\pi|\langle u_{2s}(1)Y_0^0(1)u_{2p}(2)Y_1^1(2)|(1/r_{12})|a_{1s}(1)Y_0^0(1)b_{kp}(2)Y_1^1(2)+a_{1s}(2)Y_0^0(2)b_{kp}(1)Y_1^1(1)\rangle|^2\rho(E_0).\end{aligned} \tag{28}$$

As a second example, consider the $(1s,2s,2p)\ {}^4P_{5/2}\rightarrow(1s^2,kf)\ {}^2P_{5/2}$ transition in lithium.

$$|\varphi_i\rangle=\frac{1}{\sqrt{6}}\sum_{\mathcal{P}}(-1)^{\mathcal{P}}\mathcal{P}[u_{1s}(1)Y_0^0(1)u_{2s}(2)Y_0^0(2)u_{2p}(3)Y_1^1(3)][\chi_{1/2}(1)\chi_{1/2}(2)\chi_{1/2}(3)], \tag{29}$$

where $\mathcal{P}$ is the permutation operator and the orbitals, picked real, are determined by the Hartree-Fock equations

$$T_1u_{1s}(1)-(3/r_1)u_{1s}(1)+f_0(1)u_{1s}(1)+g(1)u_{1s}(1)-\delta(1)u_{2s}(1)-\eta(1)u_{2p}(1)+\lambda_{12}u_{2s}(1)=-\lambda_1u_{1s}(1), \tag{30a}$$

$$T_2u_{2s}(2)-(3/r_2)u_{2s}(2)+h_0(2)u_{2s}(2)+g(2)u_{2s}(2)-\delta(2)u_{1s}(2)-\gamma(2)u_{2p}(2)+\lambda_{12}u_{1s}(2)=-\lambda_2u_{2s}(2), \tag{30b}$$

$$T_3u_{2p}(3)-(3/r_3)u_{2p}(3)+f_1(3)u_{2p}(3)+h_1(3)u_{2p}(3)-\eta(3)u_{1s}(3)-\gamma(3)u_{2s}(3)=-\lambda_3u_{2p}(3); \tag{30c}$$

where

$$g(1)=\int\int u_{2p}(2)Y_1^1(2)^*Y_0^0(1)\frac{1}{r_{12}}u_{2p}(2)Y_0^0(1)Y_1^1(2)d\mathbf{r}_2d\Omega_1, \tag{31a}$$

$$f_i(1)=\int\int u_{2s}(2)Y_0^0(2)Y_i^i(1)^*\frac{1}{r_{12}}u_{2s}(2)Y_0^0(2)Y_i^i(1)d\mathbf{r}_2d\Omega_1, \tag{31b}$$

$$h_i(1)=\int\int u_{1s}(2)Y_0^0(2)Y_i^i(1)^*\frac{1}{r_{12}}u_{1s}(2)Y_0^0(2)Y_i^i(1)d\mathbf{r}_2d\Omega_1, \tag{31c}$$

$$\delta(1)=\int\int u_{1s}(2)Y_0^0(2)Y_0^0(1)\frac{1}{r_{12}}u_{2s}(2)Y_0^0(2)Y_0^0(1)d\mathbf{r}_2d\Omega_1, \tag{31d}$$

$$\eta(1)=\int\int u_{2p}(2)Y_1^1(2)^*Y_0^0(1)\frac{1}{r_{12}}u_{1s}(2)Y_0^0(2)Y_1^1(1)d\mathbf{r}_2d\Omega_1, \tag{31e}$$

$$\gamma(1)=\int\int u_{2p}(2)Y_1^1(2)^*Y_0^0(1)\frac{1}{r_{12}}u_{2s}(2)Y_0^0(2)Y_1^1(1)d\mathbf{r}_2d\Omega_1, \tag{31f}$$

and λ_{12} is the Lagrange multiplier which insures the orthogonality of u_{1s} and u_{2s}. Note that then multiplying Eq.

(30a) by $u_{2s}(1)$ and Eq. (30b) by $u_{1s}(2)$ and subtracting

$$\begin{aligned}\int u_{2s}(1)[(f_0(1)g(1))u_{1s}(1)-\delta(1)u_{2s}(1)-\eta(1)u_{2p}(1)]r_1^2dr_1&\\ =\int u_{1s}(2)[(h_0(2)+g(2))u_{2s}(2)-\delta(2)u_{1s}(2)-\gamma(2)u_{2p}(2)]r_2^2dr_2&\equiv C. \qquad (31\text{g})\end{aligned}$$

The form of the "final" state is

$$\begin{aligned}|\varphi_f\rangle=\frac{1}{\sqrt{12}}\sum_{\mathcal{P}}(-1)^{\mathcal{P}}\mathcal{P}[b_{kf}(1)[-(6/7)^{1/2}Y_3{}^3(1)\chi_{-1/2}(1)+(1/7)^{1/2}Y_3{}^2(1)\chi_{1/2}(1)]&\\ \times a_{1s}(2)a_{1s}(3)Y_0{}^0(2)Y_0{}^0(3)(1/\sqrt{2})[\chi_{1/2}(2)\chi_{-1/2}(3)-\chi_{-1/2}(2)\chi_{1/2}(3)]],& \qquad (32)\end{aligned}$$

where the Clebsch-Gordan coefficients have been used to get a $J=\frac{5}{2}$ state. Since there are no f electrons in the initial state, we can choose an H_0 to give any solution we wish for b_{kf}. Thus we choose the b_{kf} to be Hartree-Fock, i.e., the solution to

$$T_1c_{1s}(1)-(3/r_1)c_{1s}(1)+f'(1)c_{1s}(1)+g'(1)c_{1s}(1)-\tfrac{1}{2}h'(1)b_{kf}(1)=-\lambda c_{1s}(1), \qquad (33\text{a})$$

$$T_2b_{kf}(2)-[3/r_2-2f'(2)]b_{kf}(2)-h'(2)c_{1s}(2)=\epsilon b_{kf}(2); \qquad (33\text{b})$$

where

$$f'(1)=\int\int c_{1s}(2)Y_0{}^0(2)Y_0{}^0(1)\frac{1}{r_{12}}c_{1s}(2)Y_0{}^0(2)Y_0{}^0(1)d\mathbf{r}_2d\Omega_1, \qquad (34\text{a})$$

$$g'(1)=\int\int b_{kf}(2)Y_3{}^3(2)^*Y_0{}^0(1)\frac{1}{r_{12}}b_{kf}(2)Y_3{}^3(2)Y_0{}^0(1)d\mathbf{r}_2d\Omega_1, \qquad (34\text{b})$$

$$h'(1)=\int\int b_{kf}(2)Y_3{}^3(2)^*Y_0{}^0(1)\frac{1}{r_{12}}c_{1s}(2)Y_0{}^0(2)Y_3{}^3(1)d\mathbf{r}_2d\Omega_1. \qquad (34\text{c})$$

We can then write H_0 for this problem as

$$H_0=\sum_{i=1}^{3}\left(T_i-\frac{3}{r_i}+Q(i)+P(i)\right)-K, \qquad (35)$$

where K is the difference between $-\lambda_1-\lambda_2-\lambda_3$ and the Hartree-Fock energy E_0 of $|\varphi_i\rangle$;

$$P(i)=|Y_3{}^3(i)\rangle(2f'(i)-h'(i)c_{1s}(i)/b_{kf}(i))\langle Y_3{}^3(i)|+|Y_3{}^2(i)\rangle(2f'(i)-h'(i)c_{1s}(i)/b_{kf}(i))\langle Y_3{}^2(i)|, \qquad (36)$$

$$\begin{aligned}Q(i)=&[g(i)+f_0(i)]|u_{1s}(i)Y_0{}^0(i)\rangle\langle u_{1s}(i)Y_0{}^0(i)|+|u_{1s}(i)Y_0{}^0(i)\rangle\langle u_{1s}(i)Y_0{}^0(i)|[g(i)+f_0(i)]\\ &-|u_{1s}(i)Y_0{}^0(i)\rangle[\langle u_{1s}(j)Y_0{}^0(j)|g(j)+f_0(j)|u_{1s}(j)Y_0{}^0(j)\rangle-\langle u_{2s}(j)|\delta(j)|u_{1s}(j)Y_0{}^0(j)\rangle\\ &-\langle u_{2p}(j)Y_0{}^0(j)|\eta(j)|u_{1s}(j)Y_0{}^0(j)\rangle]\langle u_{1s}(i)Y_0{}^0(i)|+[g(i)+h_0(i)]|u_{2s}(i)Y_0{}^0(i)\rangle\langle u_{2s}(i)Y_0{}^0(i)|\\ &+|u_{2s}(i)Y_0{}^0(i)\rangle\langle u_{2s}(i)Y_0{}^0(i)|[g(i)+h_0(i)]-|u_{2s}(i)Y_0{}^0(i)\rangle[\langle u_{2s}(j)Y_0{}^0(j)|[g(j)+h_0(j)]|u_{2s}(j)Y_0{}^0(j)\rangle\\ &-\langle u_{1s}(j)Y_0{}^0(j)|\delta(j)|u_{2s}(j)Y_0{}^0(j)\rangle-\langle u_{2p}(j)Y_0{}^0(j)|\gamma(j)|u_{2s}(j)Y_0{}^0(j)\rangle]\langle u_{2s}(i)Y_0{}^0(i)|\\ &+|Y_1{}^1(i)\rangle[h_1(i)+\langle u_{1s}(j)Y_1{}^1(j)|\eta(j)|u_{2p}(j)Y_1{}^1(j)\rangle+f_1(j)+\langle u_{2s}(j)Y_1{}^1(j)|\gamma(j)|u_{2p}(j)Y_1{}^1(j)\rangle]\langle Y_1{}^1(i)|\\ &+[\lambda_{12}-C-\delta(i)]|u_{2s}(i)Y_0{}^0(i)\rangle\langle u_{1s}(i)Y_0{}^0(i)|-|u_{1s}(i)Y_0{}^0(i)\rangle\langle u_{2s}(i)Y_0{}^0(i)|\delta(i)\\ &+[\lambda_{12}-C-\delta(i)]|u_{1s}(i)Y_0{}^0(i)\rangle\langle u_{2s}(i)Y_0{}^0(i)|-|u_{2s}(i)Y_0{}^0(i)\rangle\langle u_{1s}(i)Y_0{}^0(i)|\delta(i)\\ &-\eta(i)|u_{1s}(i)Y_1{}^1(i)\rangle\langle u_{2p}(i)Y_1{}^1(i)|-|u_{2p}(i)Y_1{}^1(i)\rangle\langle u_{2s}(i)Y_1{}^1(i)|\eta(i)\\ &-\eta(i)|u_{2p}(i)Y_0{}^0(i)\rangle\langle u_{2s}(i)Y_0{}^0(i)|-|u_{1s}(i)Y_0{}^0(i)\rangle\langle u_{2p}(i)Y_0{}^0(i)|\eta(i)\\ &-\gamma(i)|u_{2s}(i)Y_1{}^1(i)\rangle\langle u_{2p}(i)Y_1{}^1(i)|-|u_{2p}(i)Y_1{}^1(i)\rangle\langle u_{2s}(i)Y_1{}^1(i)|\gamma(i)\\ &-\gamma(i)|u_{2p}(i)Y_0{}^0(i)\rangle\langle u_{2s}(i)Y_0{}^0(i)|-|u_{2s}(i)Y_0{}^0(i)\rangle\langle u_{2p}(i)Y_0{}^0(i)|\gamma(i), \qquad (37)\end{aligned}$$

C, being defined by (31g). Then, solving $H_0|\varphi_f\rangle=E_0|\varphi_f\rangle$, we find that a_{1s} is an eigenfunction of the same Hermitian operator as u_{1s}, and, since neither have any nodes, they cannot be orthogonal. Thus, they must have the same eigenvalue, λ_1. Hence $a_{1s}=u_{1s}$. b_{kf} is then the solution to (33b) with $\epsilon=\lambda_1-\lambda_2-\lambda_3$. The rate is then

$$\begin{aligned}R=2\pi\alpha^4|\langle u_{2s}(2)Y_0{}^0(2)u_{2p}(3)Y_1{}^1(3)\chi_{1/2}(2)\chi_{1/2}(3)|(\mathbf{s}_2\cdot\mathbf{s}_3/r_{23}{}^3)&\\ -3[(\mathbf{s}_2\cdot\mathbf{r}_{23})(\mathbf{s}_3\cdot\mathbf{r}_{23})/r_{23}{}^5]|b_{kf}(3)[-(6/7)^{1/2}Y_3{}^3(3)\chi_{-1/2}(3)+(1/7)^{1/2}Y_3{}^2(3)\chi_{1/2}(3)]u_{1s}(2)Y_0{}^0(2)\chi_{-1/2}(2)&\\ -b_{kf}(2)[-(6/7)^{1/2}Y_3{}^3(2)\chi_{-1/2}(2)+(1/7)^{1/2}Y_3{}^2(2)\chi_{1/2}(2)]u_{1s}(3)Y_0{}^0(3)\chi_{-1/2}(3)\rangle|^2\rho(E_0),& \qquad (38)\end{aligned}$$

TABLE I. Auto-ionization rates in units of sec^{-1}. The $^2P_+$ and $^2P_-$ refer to the higher and lower ^2P state arising from the $(1s,2s,2p)$ configuration.

State	This paper	Burke, McVicar, and Smith[a]	Bransden and Dalgarno[b]	Cooper[c]	Propin[d]	Ta-You Wu[e]	Experiment[f]
$(2s)^2\ ^1S$ He	2.3×10^{14}	2.40×10^{14}	7×10^{14}		3.51×10^{14}	4×10^{14}	
$(2s,2p)\ ^1P$ He	8.1×10^{13}	6.2×10^{13}	1×10^{15}	1.4×10^{14}	3.84×10^{13}		6×10^{13}
$(2s,2p)\ ^3P$ He	1.5×10^{13}	1.63×10^{13}	8×10^{14}	6.6×10^{13}	5.01×10^{13}	5×10^{13}	
$(1s,2s,2p)\ ^2P_+$ Li	1.7×10^{13}				2.55×10^{14}		
$(1s,2s,2p)\ ^2P_-$ Li	0.60×10^{13}						
$(1s,2s,2p)\ ^4P_{5/2}$ Li	1.7×10^{5}						1.96×10^{5}

[a] Reference 6.
[b] Reference 5.
[c] Reference 2.
[d] References 3 and 4.
[e] Reference 1.
[f] References 7 and 8.

the rest of $H-H_0$ giving no contribution since $\Delta L=2$ in this transition.

This formulation exhibits two important features: Because of the orthogonality of the single-electron orbitals, and the fact that an electron with quantum numbers (n,l) in the initial state will have the same wave function as an (n,l) electron in the "final" state, only the orbitals of the electrons actually undergoing a transition will contribute to the rate. Further, since H_0 contains only single-particle interactions, the only nonvanishing contribution to the rate of $H-H_0$ is the two-electron part of H.

V. RESULTS AND DISCUSSIONS

In Table I (which cites Refs. 7 and 8) the results of our calculations are shown along with those of several other calculations and experiments for comparison. The fact that our results in helium agree best with those of Burke, McVicar and Smith,[6] who did a scattering-theory close-coupling-approximation calculation, indicates the accuracy of our results. Our result for the $(1s,2s,2p)\ ^4P_{5/2}$ state of lithium lies within the limit of error of 20% of the value obtained by Feldman and Novick.[7] Further, the measured value is probably slightly higher than the true value because some shorter lived atoms ($J=\frac{3}{2}, \frac{1}{2}$) reach the detector.

The accuracy of this calculation depends upon how good an approximation the Hartree-Fock initial-state wave function is to the true initial state, i.e., it depends on the amount of configuration interaction of the initial state with other discrete states. Thus it cannot be applied to $(2s,3p)\ ^1P$ or $(3s,2p)\ ^1P$, for example, since they are almost degenerate and the true wave functions are linear combinations of those of the two configurations. The fact that our method cannot handle configuration-interaction wave functions or those containing correlation terms is its major limitation.

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[7] P. Feldman and R. Novick, in *Atomic Collision Processes* (North-Holland Publishing Company, Amsterdam, 1964), p. 201.

[8] U. Fano, Phys. Rev. **124**, 1866 (1961).