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Many-electron effects in and operator forms for electron quadrupole transition probabilities

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A many-electron theory for electric-quadrupole transitions is proposed. Correlated length and velocity results are evaluated for the transitions Li I $2s \rightarrow 3d$, $2p \rightarrow 3p$; Cs I $6s \rightarrow 5d$, Ti III $3d^2\,{}^3F \rightarrow 3d^2\,{}^3P$, $3d4s\,{}^3D$; Cu II $3d^{10}\,{}^1S \rightarrow 3d^9 4s\,{}^1D$; C III $2s^2\,{}^1S \rightarrow 2p^2\,{}^1D$, $2s3d\,{}^1D$, and Zn I $4s^2 \rightarrow 4s4d\,{}^1D$, and found to be in good agreement. For Cs I, relativistic effects were also large.

I. INTRODUCTION

Formerly, experimental and observational interest in electric-quadrupole transition probabilities has been mainly confined to those involving lines within $2p^q$, $3p^q$, and $3d^q$ configurations. Theoretical emphasis has been on these configurations and the alkalis. Almost all[1-16] theoretical treatments have been based on an independent-particle model, and the bulk have used experimental structure information to introduce relativistic (e.g., intermediate coupling) and many-body effects. Exceptions to these comments are the work of Nicolaides *et al.*,[17] who did correlated nonrelativistic all-electron calculations for $2p^q$ species and that of McCavert and Trefftz[18] who did frozen-core plus two electron multiconfigurational Hartree-Fock calculations for Ba I $6s^2\,{}^1S - 5d6s\,{}^1D$. Reviews of these calculations have been made by Garstang,[19] Layzer and Garstang,[20] and Fuhr, Miller, and Martin.[21] Recently, there has been a considerable increase in the frequency of laboratory observation[22,23] and measurement[7,12,24-27] of $E2$ transitions. Measurement, although formidable due to the small absorption cross sections, has become much more accurate (~30%), as our table of Cs I results will indicate. Furthermore, these transitions are integral parts of modern laser and plasma technology.

So we are led to expect that in the future we will have to be able to treat $E2$ transitions between an arbitrary pair of states; and we may ask whether the current theoretical state of the art is adequate to do this. Several major questions arise: (1) What is the general role of many-electron effects—which we may decompose, for the Hartree-Fock (HF) results only, into nonorthonormality (NON) and correlation (treated by configuration interaction (CI) methods here)? Do these remain small (or at least not violate an independent-particle formalism) as they seem to be for most of the transitions studied earlier? If not, what are the principal configurations affecting $E2$? (2) Which operator form—length or velocity—is preferred, i.e., gives the most accurate and dependable answers? (3) What, if any, qualitative changes occur in progressing from atoms with simple structure (e.g., He–Ar) to those with more complex structures (e.g., transition metals)? (4) What role do relativistic effects play?

In the remaining parts of this paper, we will discuss in detail questions (1)–(3). Relativistic effects will only be included in *ad hoc* ways. To date, there remains no satisfactory way to deal with both relativity and correlation. Specific results are given for C III $2s^2\,{}^1S - 2p^2$, $2s3d\,{}^1D$; Zn I $4s^2\,{}^1S - 4s4d\,{}^1D$; Cu II $3d^{10} - 3d^9 4s\,{}^1D$, Ti III $3d^2\,{}^3F - 3d^2\,{}^3P$, Cs I $6s - 5d$; Ti III $3d^2\,{}^3F - 3d4s\,{}^3D$; Li I $2s - 3d$, $2p - 3p$. For the C, Zn transitions, many electron effects are large, for those in Cu$^+$, Ti^{++} ${}^3F - {}^3P$, moderate, and in Ti^{++} ${}^3F - {}^3D$ and Li, small. Certain rules are proposed to allow *a priori* estimation of when many electron effects can be large. Concerning operator choice, we find that the velocity operator is best avoided in dealing with no electron jumps due to the considerable cancellations which may appear in the radial velocity integral.

In Sec. II, we present the many-electron $E2$ formalism in terms of arbitrary CI wave functions; in Sec. III, we deal with the wave function construction, developing an approach (FOTOS/$E2$) which successfully predicts the configurations (always a small number) that need to be retained to produce good quadrupole transition matrix elements. In Sec. IV, the results are given, and Sec. V discusses our findings.

II. MANY-ELECTRON $E2$ TRANSITION PROBABILITY FORMULAS

The transition probability for spontaneous emission, A_{ki}, from state $k(\alpha_k S L_k J_k)$ to state $i(\alpha_i S L_i J_i)$ is given by[28]

$$A_{ki} = \frac{1.679 \times 10^{18}}{(2J_k + 1)\lambda^5} S_{E2}(k \rightarrow i)\,, \tag{1}$$

where A_{ki} is in sec^{-1}, λ is in Å, and S_{E2}, the line strength, is in atomic units (a.u.). The N-electron E_2 transition operator, $T^{(2)}$, is a sum of one-electron tensor operators of rank 2, $t^{(2)}(i)$, whose five components are denoted with a subscript Q or q, i.e., $T_Q^{(2)}$, $t_q^{(2)}(i)$. The line strength is then given by

$$S_{E2}(k\rightarrow i)=\sum_{Q=-2}^{+2}\;\sum_{M_J^k=-J_k}^{+J_k}\;\sum_{M_J^i=-J_i}^{+J_i}|\langle k|T_Q^{(2)}|i\rangle|^2 . \qquad (2)$$

As we shall be using states for the levels (J_i, J_k) constructed from LS coupled functions, it is possible to relate all (J_k, J_i) combinations to a single LSM_LM_S matrix element using the Wigner-Eckart theorem.[29] Specifically, we have

$$S_{E2}(\alpha_kSL_kJ_k\rightarrow\alpha_iSL_iJ_i)=(2J_i+1)(2J_k+1)\left[\begin{Bmatrix}J_k & L_k & S\\ L_i & J_i & 2\end{Bmatrix}^2\Big/\begin{pmatrix}L_k & 2 & L_i\\ -L_k & L_k-L_i & L_i\end{pmatrix}^2\right]$$
$$\times|\langle\alpha_kSM_s^k=SLM_L^k=L_k|T_{L_k-L_i}^{(2)}|\alpha_iSM_s^i=SLM_L^i=L_i\rangle|^2 . \qquad (3)$$

The last term is the "line strength" N-electron integral in the LM_LSM_S scheme, with $M_L=L$, $M_S=S$ which is the "natural" coupling of the many-electron wave function (see Sec. III). The $\{\,\}$ is a $6j$ and the ( ) a $3j$ symbol,[30] in which are embedded the familiar[19] N-electron selection rules, e.g., the triads $(J_i, J_k, 2)$, $(L_i, L_k, 2)$ must satisfy the triangle inequality. We have already anticipated the spinlessness of $T^{(2)}$ by requiring $S_k=S_i=S$. Since this operator is also an even one, both states will also have the same parity; also $\Delta M_J=0$, ±1, ±2.

A. Length form of the operator

The conventional form of the operator employed is the length one. Frequently (e.g., Garstang[19]) this has been expressed as a dyadic: Here we use an equivalent form

$$t_{L_k-L_i}^{2l}=\left(\frac{8\pi}{15}\right)^{1/2}Y_{2,L_k-L_i}(\Omega) \qquad (4)$$

also used by others (e.g., Boyle and Murray[1]). The $Y_{2,L_k-L_i}(\Omega)$ is a spherical harmonic normalized according to the convention of Condon and Shortly.[31]

In addition to the operator itself, we shall need its one-electron matrix elements. Using spin orbitals as one-electron functions, viz $nlmm_s=R_{nl}(r)Y_{lm_l}(\Omega)\eta_{m_s}$ we have

$$\langle n'l'm'm_s|t_{L-L'}^{2l}|nlmm_s\rangle$$
$$=W_{L-L'}(l'm';lm)\int_0^\infty R_{nl}R_{n'l'}r^4dr , \qquad (5a)$$

where

$$W_{L-L'}(l'm';lm)=(\tfrac{2}{3})^{1/2}[(2l+1)(2l'+1)]^{1/2}(-1)^{m'}$$
$$\times\begin{pmatrix}l' & 2 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l' & 2 & l\\ -m' & L-L' & m\end{pmatrix}. \qquad (5b)$$

B. Velocity form of the transition operator

The subject of alternative operator forms divides itself into three parts: (1) generating a form for the electron-photon interaction consistent with formal theory[32,33]; (2) creating formally equivalent transition operator forms through use of hypervirial theorems,[1,34,35] i.e., $\dot{X}=[H,X]/\Delta E$, where ΔE is the N-electron energy difference, X, $\dot{X}$ the two operator forms, and H the Hamiltonian used to generate the N-electron wave functions. This prescription presumes of course that we deal with exact wave functions of H. Finally, (3) judging which of the alternative operator forms is most accurate in computational practice.

From our viewpoint, results from different operator forms will only disagree because we have not obtained sufficiently accurate wave functions. As has been noted many times (e.g., Nicolaides and Beck[36]), agreement does *not* imply correctness; one can not even be certain the correct value lies anywhere near the common result. Errors in any of the above three stages can be responsible for this situation. Given the considerable latitude for error, we can anticipate that *a priori* judgements of the accuracy of a given result will remain an insoluble problem.

Our approach here is to use the length form of the N-electron operator given above [Eq. (4)] as the one generated from interaction theory and apply the hypervirial theorem with the nonrelativistic Hamiltonian as did Boyle and Murray[1] and McCavert and Trefftz[18] to generate an N-electron velocity equivalent. The one-electron matrix element of this operator is given below:

$$\langle n'l'm_l'm_s \,|\, t^{2v}_{L\text{-}L'} \,|\, nlm_lm_s\rangle = \frac{2}{\Delta E}\, W_{L\text{-}L'}(l'm';lm)\left(-\int_0^\infty r^3 dr\, R_{n'l'}\frac{dR\,nl}{dr} + B_{l',l}\int_0^\infty dr\, P_{n'l'}P_{nl}\right) \tag{6a}$$

with

$$B_{l',l} = \begin{cases} -3/2, & l' = l \\ l, & l' = l+2 \\ -(l+1), & l' = l-2 \end{cases} \tag{6b}$$

where ΔE is the N-electron nonrelativistic energy difference given in a.u. As part of our approximation, we shall obtain ΔE from experiment, approximately removing relativistic effects from it, when they are large. This implies that the "exact" nonrelativistic Hamiltonian and wave functions are used for this part, whereas for the transition matrix element $\langle \underline{\psi}_{NR}(k)\,|\,T^{(2)}\,|\underline{\psi}_{NR}(i)\rangle$ we argue that approximate solutions (see Sec. III) to the nonrelativistic Hamiltonian are satisfactory. This approach will allow us to restrict the calculation of $\underline{\psi}_{NR}$ to just a few configurations. *Ad hoc* ways of introducing relativistic effects are discussed in the Sec. IV A dealing with the Cs I transition.

C. Nonorthonormality (NON)

We choose to use state specific one-electron functions to reduce the size of the CI expansions. This means that NON effects arise when dealing with off-diagonal properties. These reduce to the treatment of NON between two Slater determinants (Δ), which we evaluate using the methods of King *et al.*[37]

Let $\underline{D}$ be the overlap matrix whose elements are

$$D_{ij} = \int b_i^* a_j d\tau\,, \tag{7}$$

where b_i is the ith spin orbital in Δ_b, etc. Solve the eigenvalue problems below, using standard Hermitian diagonalizers:

$$(\underline{D}^\dagger \underline{D})\underline{V} = \underline{V}\underline{\Lambda}\,, \tag{8a}$$

$$(\underline{D}\,\underline{D}^\dagger)\underline{U} = \underline{U}\underline{\Lambda}\,, \tag{8b}$$

where $\underline{D}^\dagger$ is the adjoint of $\underline{D}$.

If we let $d_{ii} \equiv \Lambda_{ii}^{1/2}$, $d_{ii} \geq d_{jj} \geq 0 (i<j)$, then for an N-electron operator which is a sum of arbitrary one-electron operators, viz; $\Omega = \sum_{i=1}^N \omega(i)$ we have

$$\langle \Delta_b\,|\Omega\,|\Delta_a\rangle = (\det \underline{U})(\det \underline{V}^\dagger)\sum_{i=1}^N \langle \hat{b}_i\,|\omega\,|\hat{a}_i\rangle \prod_{j\neq i}^N d_{jj}\,, \tag{9}$$

where $\underline{\hat{b}}$ and $\underline{\hat{a}}$ are linear transformations of the original spin orbitals, viz.,

$$\underline{\hat{a}} = \underline{a}\,\underline{V}\,, \tag{10a}$$

$$\underline{\hat{b}} = \underline{b}\,\underline{\tilde{U}}\,, \tag{10b}$$

These formulas, while correct, are fairly expensive to evaluate. Certain simplifications were made to them for the electric-dipole case[38] and for the electric-quadrupole case.[17]

However, even the above simplifications left the treatment of NON an expensive computational bottleneck. Here we outline a procedure which has effected the complete removal of NON as a bottleneck. This has been applied to $E1$ (Nicolaides and Beck[39]) and $E2$ transitions (this work). The streamlining is accomplished in several steps: (1) *a priori* recognition and subsequent discarding of configurational and determinantal matrix elements which are identically zero due to symmetry (our NON is entirely radial in nature). To do this, we first form pseudospin orbitals and pseudoconfigurations by neglecting the principle quantum numbers. For example, the pseudoconfigurational equivalent of $1s^2 2s3d$ is s^3d. The determinant $1s0\alpha 1s0\beta 2s0\alpha 3d{+}2\alpha$ would be reduced to $(s0\alpha)^2(s0\beta)(d{+}2\alpha)$. These pesudoconfigurations (determinants) are then tested to see if they satisfy the relevant *one*-electron selection rules. If they do not, they are discarded. A common determinantal survival figure is about 1 in 10, e.g., $\leq 10\,000$ interactions survive out of 100 000. (2) The deep core radial functions are state independent and thus can be shown to make no contribution to the matrix element. So we treat something less than all N electrons and something more than just the "active" electrons. (3) If the two determinants differ in one and only one pseudospin orbital, then we begin by making the reduction of Westhaus and Sinanoğlu[38] as it applies here (see also Nicolaides *et al.*[17]). Owing to the ordering of the d_{ii}, and our assumption, d_{NN} is zero. For a nonzero result, we must restrict $i=N$ in Eq. (9). Furthermore, these authors showed[38] that

$$(\det \underline{U})(\det \underline{V}^\dagger)\prod_{j=1}^{N-1} d_{jj} = \det(\underline{D}')\,, \tag{11a}$$

where

$$D'_{ij} = D_{ij} + U_{iN}V_{jN}^*\,. \tag{11b}$$

Hence

$$\langle \Delta_b\,|\Omega\,|\Delta_a\rangle = \det(\underline{D}')\langle \hat{b}_N\,|\omega\,|\hat{a}_N\rangle\,, \tag{12}$$

which means we need only obtain the lowest root of $DD^\dagger$ and $D^\dagger D$, not all roots (which cuts down diagonalization time). But it is possible to avoid diagonalization altogether,[39] since we already know our eigenvalue (= 0), and can obtain the eigenvectors by solving a small system of linear equations for the components of U_N and V_N belonging to the symmetry block of the jumping pseudo-spin orbital. With these steps, the problem of NON becomes extremely tractable. Calculation times for A_Q are 1–15 min on a DEC 2060.

D. NON to first order

Our NON calculations are done to all orders. However, in order to analyze the effects of NON, it is useful to look at its first-order effects which are of two types: (1) deviation of normalization integrals from 1, (2) deviation of orthogonality integrals from zero. A first-order NON expression would contain all terms having a single normalization or orthogonality integral.

As an example consider the LI I $1s^2 2s \leftarrow \bar{1}s^2\bar{3}d$ transition. The determinants involved are $(1s\alpha 1s\beta 2s\alpha)$ and $(1\bar{s}\alpha\bar{1}s\beta 3\bar{d}2\alpha)$, where the bars are used to denote the state dependence of the radial functions. The dipole matrix element is then

$$\langle A(1s\alpha 1s\beta 2s\alpha)\,|\vec{r}^{\,2}|\,A(1\bar{s}\alpha 1\bar{s}\beta 3\bar{d}2\alpha)\rangle ,$$

which to first order is

$$\begin{aligned}&\langle 1s\alpha\,|1\bar{s}\alpha\rangle\langle 1s\beta\,|\bar{1}s\beta\rangle\langle 2s\alpha\,|r^2|\,3\bar{d}2\alpha\rangle - \langle 2s\alpha\,|1\bar{s}\alpha\rangle\langle 1s\beta\,|1\bar{s}\beta\rangle\langle 1s\alpha\,|r^2|\,3\bar{d}2\alpha\rangle\\ &\quad = \langle 1s\,|1\bar{s}\rangle^2\langle 2s\alpha\,|\vec{r}^{\,2}|\,3\bar{d}2\alpha\rangle - \langle 2s\,|1\bar{s}\rangle\langle 1s\,|1\bar{s}\rangle\langle 1s\alpha\,|\vec{r}^{\,2}|\,3\bar{d}2\alpha\rangle\end{aligned}$$

(to get the second term of the right-hand side we have performed one interchange in the first; at this stage we must maintain spin orbitals, as only ones with the same $lm_l m_s$ can be rotated). Technically, this should be further simplified to get the first-order results, but this form is easiest to work with. In Sec. IV, where the effects of NON on the HF length result are given, we compare the above result to that for full orthonormality ($\langle nl\,|\bar{n}l\rangle = \delta n,\bar{n}$ in the above).

III. FIRST-ORDER THEORY OF OSCILLATOR STRENGTHS FOR $E2$ (FOTOS/$E2$)

We develop the analysis for $E2$ along the same lines as that for $E1$.[39,40] For each state, there is one or possibly two (see Beck and Nicolaides[41] for examples) dominant configuration(s) which are used to construct the reference function, Φ. To predict the correlation configurations which are to appear in the *other* state, we (1) apply the quadrupole operator of equation (4) to the above pseudoconfiguration, using the selection rules of equation (5), viz, $s\rightarrow d$, $p\rightarrow p+f$, $d\rightarrow s+d+g$, which then yields all pseudoconfigurations of the *other* state which survive, to first order, in the quadrupole matrix element. In reducing Φ to its pseudoconfiguration, subshells assigned to the deep core (see Sec. II) are neglected (and throughout the analysis). In abstract terms, if the initial pseudoconfiguration is $s^k p^m d^n$, application of the $E2$ operator creates the pseudoconfigurations

$$s^k p^m d^n X E2 \rightarrow \begin{cases} s^{k-1}p^m d^{n+1}(s\rightarrow d)\\ s^k p^m d^n (p\rightarrow p;\, d\rightarrow d)\\ s^k p^{m-1} d^n f\,(p\rightarrow f)\\ s^{k+1}p^m d^{n-1}(d\rightarrow s)\\ s^k p^m d^{n-1} g\,(d\rightarrow g)\end{cases} \qquad (13)$$

and, (2) we then replace the newly created pseudoconfigurations with actual configurations, by expanding the pseudosubshells in terms of actual subshells.

Before carrying out this second step, we must review the process by which the full first-order correlation function is constructed[41,42] for any arbitrary property, for we shall not permit FOTOS/$E2$ to produce any configurations which are not part of this function. In essence, the full correlation function just contains all single- and double-subshell excitations from the configurations in the reference function. For most properties, there will be several subshells in the deep core, i.e., kept frozen. We excite from configurations rather than determinants as in the past[43] in order to ensure production of L^2, S^2 eigenstates. This reduces the errors in energetics, transition probabilities, etc.

More critically, we divide up the radial space into the Fermi sea (FS) and its orthogonal complement, the virtual space. The Fermi sea consists of all radials in Φ and any additional radials nearly degenerate with them. Specific examples appear in Sec. IV, while surveys may be found elsewhere.[42] Designating occupied *FS* subshells as s_i, open *FS* subshells as $\bar{s}_i$ (occupations less than $4l+2$), and the orthogonal virtual subshells as v_i, the full first-order correlation function may be written schematically as a sum of five parts:

$s_i \rightarrow \bar{s}_i$, (internal polarization) (14a)

$s_i s_j \rightarrow \bar{s}_i\bar{s}_j$, (internal) (14b)

$s_i \rightarrow v_i$, (virtual polarization) (14c)

$s_i s_j \rightarrow \bar{s}_i v_j$, (hole-virtual) (14d)

$s_i s_j \rightarrow v_i v_j$, (bivirtual). (14e)

The above divisions have both computational and conceptual significance; for example, for many one-electron properties of ionized species[41,42,44] we need no excitations of the type (14e). Further examples are given elsewhere.[39,42,45]

First-order perturbation theory, which has dictated the *form* of the correlation function, also serves to limit the virtual symmetries of sections (14c) and (14d) to $3l_{\text{MFS}}$, where l_{MFS} is the maximum Fermi sea azimuthal quantum number. Computational practice suggests such a limit is adequate for part (14e) as well.

The unknowns of the correlation function are the radial functions—FS and virtual—and the CI coefficients. We determine the FS radials using either the numerical restricted HF (RHF) code of Froese-Fischer[46] or the matrix code of Roos *et al.*,[47] which is based on Roothaan's work.[48] Generally, FS radials not appearing in the reference function, Φ, are obtained by separate single configurational RHF calculations, and then orthogonalized, if necessary, to those in Φ. Virtual radial functions, on the other hand, are determined as part of the variational CI process. Prior to orthogonalization, they are represented as one or two Slater orbitals (STOS) or Gaussian-type orbitals (GTOs), with unknown nonlinear parameters, i.e., exponents. These quantities can be very well estimated (to start the variational process) by forcing them to have the same $\langle r\rangle$ as that of the subshells they replace. Virtuals associated with $K,L,M,\ldots$ subshells then have very different characteristics. Once the configurations and FS radials are known, the correlation function is generated in a completely automated way by program SMART-PSI developed by the author and C. A. Nicolaides.[49]

How do the above considerations specify which configurations are to be used for $E2$? There are two general restrictions in effect: (1) No pseudoconfiguration can be mapped to a configuration which has more than two virtuals, (2) in substantionally ionized systems, we shall exclude bivirtual configurations as these would involve, when computing the quadrupole matrix element, an overlap integral with the FS of the other state, which is nearly identical to the FS of our state; hence, the overlap integral is nearly zero. Configurations producing overlaps between FS radials belonging to different shells are likewise small. To demonstrate these considerations, let us consider the example Cu $3d^{10}\,{}^1S \to 3d^9 4s\,{}^1D$. What does FOTOS/$E2$ applied to the upper state predict should be in the lower one? We will assume that $1s,\ldots,3p$ subshells belong to the deep core, i.e., remain frozen.

$$3d^9 4s \to d^9 s\ ({}^1D\text{ pseudoconfig}) \times E2\ .$$

$$\to d^{10} + d^8 s^2 + d^9 s + d^8 sg\ ({}^1S\text{ pseudoconfig})\,.$$

We take the ${}^1S$ reference function to be solely $3d^{10}$, and further assume that the active FS $= 3d$ only (any $3d$, $4s$ degeneracy effects will be adequately picked up with a v_s). With these considerations, and our earlier restrictions, we can recover the appropriate configurations:

$$d^{10} \to 3d^{10} + 3d^9 v_d + 3d^8 v_d^2\,,$$

$$d^8 s^2 \to 3d^9 v_s^2\,,$$

$$d^9 s \to \text{none:no }{}^1S\,,$$

$$d^8 sg \to 3d^8 v_s v_g\,.$$

The one major remaining question is whether any of the excluded configurations can significantly affect the coefficients or virtual radial functions of the configurations admitted by FOTOS/$E2$. If they do, they will have to be added to those we already have. Generally, we will in fact need a few such configurations. These will be of three types: (1) A few of types (14b) and (14d) representing the *largest* correlation effects. Each such configuration is generated such that all FS subshells involved in the excitation have the same principle quantum number (otherwise they will be small and can be excluded). Examples are $np^2 \to ns\,nd$; $np^2 \to ns\,v_d$. Further examples are found in Sec. IV and in previous work[45] which contains a nearly complete list. (2) Particular attention should be paid to the largest arising from the same pairs $s_i s_j$ as these admitted by FOTOS/$E2$. They are of types (14b), (14d), (14e); and (3) single excitations of the type $nl \to x_{nl}$ ($x =$ FS or v) where l is preserved, are critically important FOTOS/$E2$ configurations; they serve to correct the radial part of the HF one-electron functions in Φ. Yet these excitations are only weakly connected to Φ, because Brillouin's theorem is frequently nearly satisfied. They are in fact most directly connected to double excitations of the type $nlm'l' \to y_{n\hat{l}} z_{m'\hat{l}'}$ where $m' = n$ if possible, or at least $n \pm 1$. The matrix connecting the single and double excitations then have the structure

$$\left\langle m'l'x_{nl} \left| \frac{1}{r_{12}} \right| y_{n\hat{l}} z_{m'\hat{l}'} \right\rangle$$

which we have radially maximized because $m' \simeq n$. As an example, consider again the Cu $3d^{10}\,{}^1S$ state. The $3d \to v_d$ polarization is chiefly connected to the $3d^2$ excitations (and progressively less so to $3p3d\to$ and $3s3d\to$, etc.). The largest[50] replacements for the $3d^2$ pairs are v_f^2, v_d^2, and v_p^2, which serves to fix $\hat{l}, \hat{l}'$.

Before closing this section, it is of some interest to point out the "expensive" part of the evaluation of the correlation function. Our variational CI calculations used as an N-electron basis, symmetry adapted single-configurational functions. These are fixed linear combinations of Slater determinants which in the past,[50] we have obtained solely by direct diagonalization methods. For systems involving open d subshells such as the transition metals, however, several hundred determinants are involved, and these can no longer be generated solely by diagonalization. Instead we break the problem up, using vector coupling methods and step up or step down operators, which completely removes this as a calculational bottleneck. Details of the method will be reported elsewhere.[51] Typical calculation times for the wave functions needed in Sec. IV range from 2–10 min (DEC 2060).

IV. RESULTS

A. The alkalis

With the exception of $E2$ transitions within np^q and nd^q ground-state configurations, the alkalis have been the subject of the earliest and greatest interest. Experimentally, all laboratory measurements to date[21] have been on members of these classes. As is true in general, most theoretical work on the alkalis falls into a few categories: (1) users of the Coulomb approximation[2,12,16] as developed by Bates and Damgaard.[52] Here one solves a differential equation for the radials involved in the transition using the experimental ionization potential. In addition to the assumption of an independent particle formalism, the chief uncertainty lies in the necessary use of a cutoff radius, beyond which the inward integration ceases. An advantage of the method is that relativistic and correlation ("core-polarization") effects are partially incorporated into the model (through the ionization potential). As is usual, the method can be expected to be most accurate for one-electronlike transitions (core nl to core $n'l'$), for which the length form of the operator is to be used, and (2) partially or fully *ab initio* Hartree-Fock treatments.[1,10,13,15] The common feature is evaluation of the radial length integral $\int_0^\infty dr r^2 PP'$ using some sort of Hartree-Fock procedure.

Li I 3d→2s; 3p→2p

We study these transitions in order to permit a comparison with previous theoretical work; Li was chosen to minimize the role of correlation effects to allow a more direct comparison. No experimental results are available.

In Table I we report results obtained for the length and velocity operators obtained using both analytic and numerical RHF wave functions. The small (10^{-3}%) effects of nonorthonormality are included in these results. The analytic ones are taken from the work of Weiss.[53] Contrary to the finding of Boyle and Murray,[1] we find excellent agreement between analytic and numerical values. The only noticable difference is in the $3d \rightarrow 2s$ length value. From the values given by Boyle and Murray,[1] Caves,[2] and Table I, it appears that the numerical HF values of the first authors[1] are the ones most suspect. This changes the conclusion reached by Caves,[2] who contended the Coulomb approximation is to be preferred in this system. As Table 1 shows, no values differ by more than 4%, which should be about the size of core polarization effects. One should note the size of A_Q: electric dipole A's are on the of 10^8, configuration changing (e.g., Li) $E2$ around 10^3, and $3p^q$, $3d^q$ $E2$ transitions around 10^0.

TABLE I. Spontaneous emission probabilities, A_Q, in $\sec^{-1}$ for Li.

Method	A_Q
$2s_{1/2} \leftarrow 3d_{5/2}$ [a]	
NRHF/l [b]	261.7
NRHF/V [c]	255.4
ARHF/l [d]	255.8
ARHF/V [e]	255.3
HF/POL [f]	252.5
Model potential [g]	252.5
$2p_{3/2} \leftarrow 3p_{1/2}$ [h]	
NRHF/l [b]	27.57
NRHF/V [c]	26.76
ARHF/l [d]	27.50
ARHF/V [e]	26.75
HF/POL [f]	26.63
Model potential [g]	26.43

[a] $A_Q(2p_{3/2} \leftarrow 3p_{3/2}) \cong A_Q(2p_{1/2} \leftarrow 3p_{3/2}) \cong \frac{1}{2} A_Q(2p_{3/2} \leftarrow 3p_{1/2})$ with no fine-structure splitting, the equivalence would be exact.

[b] Numerical RHF results obtained from Froese-Fischer's program, (Ref. 46), length operator, experimental (Ref. 54) ΔE. This work.

[c] Same as (b) except velocity operator.

[d] Analytic RHF results obtained by Weiss (Ref. 53) using the Roothaan technique (Ref. 48). Length operator, experimental (Ref. 54) ΔE. This work.

[e] Same as (d) except velocity operator.

[f] Hartree-Fock-like results obtained from polarizability calculations by Sengupta (Ref. 13). In effect, the orbitals contain core-polarization effects.

[g] Results obtained by Caves (Ref. 2) using a variant of the Coulomb approximation.

[h] $A_Q(2s_{1/2} \leftarrow 3d_{3/2}) \cong A_Q(2s_{1/2} \leftarrow 3d_{5/2})$.

We should mention that the experimental energy differences as given by Moore[54] have been used to construct Table I. These values given in cm^{-1}, and were converted to eV using the relationship given in that work for ionization potentials. We then converted eV to a.u. using 1 a.u. = 27.20976 eV. These considerations are of some importance as the length form of A_Q varies as $(\Delta E)^5$ and the velocity form as $(\Delta E)^3$.

Cs I 5d → 6s

This is a transition which is being used by Nayfeh[55] in his laser photoionization studies. It has also been measured by four groups[12,56-58] with conflicting results.

Cs I is the largest system we study here; its Z is high enough to warrant careful examination to see the size of relativistic effects. We begin by looking at ΔE, which has an experimental value of 1.7973 eV ($5d_{3/2} \rightarrow 6S_{1/2}$). To estimate the effect of relativity on the gap, we do a numerical nonrelativistic ΔSCF calculation using the Froese-Fischer program,[46] and follow it with a relativistic ΔSCF Dirac-Fock calculations using the program of Desclaux.[59] We find that relativity widens the gap by 0.194 eV. This effect is quite substantial—the length scale factor (ΔE^5) nonrelativistically is 0.6 of the relativistic value. Obviously, relativistic effects can not be ignored.

For the moment, let us set this aside and treat the problem entirely nonrelativistically. Here, we are to use the nonrelativistic "experimental" energy difference of 1.6033 eV to compare the length and velocity results. We then go on to include relativistic effects in an *ad hoc* manner to provide a final value. A procedure like this is necessary because there is currently no systematic *ab initio* way of including both relativistic and correlation effects at the level required here.

The Cs I Φ configurations are $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^2\, 4p^6\, 4d^{10}\, 5s^2\, 5p^6\, (6s+5d)$. Of the thirteen subshells listed, all but $5p$, $6s$, and $5d$ will be considered part of the deep core. FOTOS/$E2$ produces the configurations $5p^6\,(6s+v_s)$, $5p^5(v_p v_d + v_d v_f + v_s v_p)$ in the ground state and $5p^6\,(5d+v_d)$, $5p^5(v_s v_p + v_s v_f + v_p v_d + v_d v_f)$ in the upper state (^2D). the upper state (^2D).

The correlated nonrelativistic (NR) results are shown in Table II. Several things are apparent. Both the NR-RHF length and velocity values are equally bad. Once again, we have a specific ex-

TABLE II. Spontaneous emission transition probability, A_Q, in sec^{-1} for Cs I $5d \rightarrow 6s$.

Upper		Lower	Method	ΔE (eV)	Length	Velocity
$5d_{3/2}$	→	$6s_{1/2}$	NR-RHF [a]	1.6033	19.32	17.98
			NR-FOTOS/$E2$ [b]	1.6033	13.83	12.96
			R-FOTOS/$E2$:A [c]	1.7973	24.5	
			C.A. [d]	1.7973	19.6	
			C.A. [e]	1.7973	20.8	
			Expt-Abs [f]	1.7973	23 ± 2	
			Expt. electron [g] impact	1.7973	49	
			Expt. emission [h]	1.7973	79	
			Expt. Hook [i]	1.7973	75	
$5d_{5/2}$	→	$6s_{1/2}$	NR-RHF [a]	1.6033	19.32	18.22
			NR-FOTOS/$E2$ [b]	1.6033	13.83	12.96
			R-FOTOS/$E2$:A [c]	1.8094	25.3	
			C.A. [d]	1.8094	20.7	
			C.A. [e]	1.8094	21.8	
			Expt-Abs [f]	1.8094	24 ± 2	
			Expt. electron [g] impact	1.8094	49	
			Expt. emission [h]	1.8094	84	
			Expt. Hook [i]	1.8094	87.5	

[a] Numerical nonrelativistic RHF results. "Exact" nonrelativistic ΔE (see text).

[b] Correlated (FOTOS/$E2$) nonrelativistic results. "Exact" nonrelativistic ΔE (see text).

[c] FOTOS/$E2$ length result using experimental (Ref. 54) ΔE.

[d] Coulomb approximation obtained by Warner (Ref. 16).

[e] Coulomb approximation obtained by Sassi (Ref. 12).

[f] Experimental result obtained by Sayer *et al.*, (Ref. 12), using absorption techniques.

[g] Experimental result obtained by Hertel and Ross (Ref. 56) using electron impact techniques.

[h] Experimental results obtained by Gridneva and Kasabov (Ref. 57) using emission techniques.

[i] Experimental results obtained by Prokofiev (Ref. 58) using the hook (anomalous dispersion) technique.

ample of good agreement between operator forms, with the result being incorrect. This can easily happen[36] for one-electronlike transitions, where the HF operator can become fairly local. Obviously, we can make no preference here as to operator form, in contrast to Cohen *et al.*[3] who prefer the velocity form for $E2$ transitions in the He isoelectronic sequence.

The correlated results are in good agreement, and differ from the RHF results by nearly 40%. NON effects are also small (10^{-3}%) here. If we accept these as close approximations to the exact nonrelativistic values, we see correlation can affect both operator forms substantially. There are two points which suggest we do this.

The results agree well, when corrected for relativity (see below), with recent experimental ones. Secondly, we have used considerable care to make sure the radial space is properly converged; omissions are likely to be at the configurational state, e.g., $5s6s$, $5s\,5d$ excitations, etc. It is to be noted that the results obtained from the theoretical energy difference need to be multiplied by about a factor of 2 to introduce the exact nonrelativistic energy. As intended, FOTOS/$E2$ successfully predicts the quadrupole matrix element without being required to simultaneously predict the energy difference. This is a recurring result throughout this work.

An analysis of the results shows that the principle correlation to the matrix element arises from $6s \rightarrow v_s$ and $5d \rightarrow v_d$. The other configurations are needed as they are the ones most strongly connected with these Brillouin-type virtual polarizations. This suggests that the problem is still fundamentally an independent particle one, with relativistic and correlation effects changing the radial functions of the outermost electron, and hence, transitions of this type should be fairly amenable to a treatment using the Coulomb approximation.

To begin the introduction of relativistic effects, we choose only the length operator as it seems more fundamental,[32] and reevaluate the correlated nonrelativistic length A_Q with fully relativistic ΔE, i.e., the experimental result. The results, designated R-FOTOS/$E2:A$, are in good agreement with the most recent experimental value[12] and two Coulomb approximation values.[12,16] Under the above procedure, if a velocity result were desired, a new $\dot{X}$ would have to be generated using, e.g., the Dirac-Breit Hamiltonian in the hypervirial theorem.

It would appear that the electron-impact results[56] (and earlier measurements[57,58]) are much too high. There seems to be a similar problem[10,60] in Na I with regard to the electron-impact method.

B. The transition metals

In 1971, Nicolaides *et al.*[17] examined many-electron effects in $2p^q$ transitions, finding them to be moderate (~17%). At that time, the role of bivirtual correlation in neutral atoms was not fully appreciated, nor was there a transition oriented configuration selection mechanism such as FOTOS/$E2$. Nonetheless, these results seem to be substantially correct.

Since that time, there has been little *ab initio* work on the role of correlation effects (see however, Sec. IV C); in particular there seems to be none on $3p^q$ and $3d^q$ transitions, aside from some early semiempirical CI used by Garstang.[4] We attempt to partially remedy this lack here by examining $3d^q$ and $3d^q \rightarrow 3d^{q-1}4s$ transitions in the transition metals; we take these up rather than those in $3p^q$ (some of which have now been measured[25,26]), because we hope more novel features will appear in them and we are currently making a study of $3d \rightarrow 4s$ excitation energies in transition metals.[61] The transitions of interest are astrophysically important and many of them have been treated[4,5,8,9] at the independent-particle level using the length operator. In general, agreement of these results with quantative (where available) astrophysical observation seems good. Nevertheless, a few critical tests would be useful in this area.

For transitions within $3d^q$ (or within any single configuration) we expect to have some difficulty with the velocity operator. Formal nonrelativistic theory assures us that as $Z \rightarrow \infty$, these transitions vanish (wave functions, etc., become hydrogenically degenerate). At the one-electron level, we have a proportionality between the radial length integral, ΔE, and the radial velocity integral, which from Eqs. (5) and (6) is

$$\Delta E \int_0^\infty R_{nl} R_{n'l'} r^4 dr \sim \left(- \int_0^\infty r^3 dr\, R_{n'l'} \frac{dR_{nl}}{dr} + B_{l'l} \int_0^\infty P_{n'l'} P_{nl\, dr} \right) \tag{15}$$

This suggests that the right-hand side must vanish faster than the length integral by a factor of ΔE. So, the radial velocity integral must involve a great deal of cancellation for transitions where ΔE is small, i.e., those with no configuration change, and hence, be difficult to evaluate and correct. We can see this explicitly if we take $nl = n'l'$ and assume the radial functions are independent of term. We have $B_{l,l} = -\frac{3}{2}$, so

$$\int_0^\infty r^3 dr\, R_{nl} \frac{dR_{nl}}{dr} = \frac{1}{2} \int_0^\infty r^3 dr \frac{dR_{nl}^2}{dr} = -\frac{3}{2} \int_0^\infty r^2 dr\, P_{nl}^2 \tag{16}$$

exactly cancels the first term. Thus, the Hartree-Fock velocity result is only nonzero in such cases due to the term dependence of the radials, which is in fact weak. Generally then, the velocity operator is not optimal for transitions within a configuration, although with some effort reliable results can be obtained with it, as our following examples suggest.

A similar analysis of cancellation effects for electric dipole transitions has been made by Layzer.[20] In practice, these are not normally a problem because the parity change forces a subshell change, and subshell degeneracy sets in at a higher Z than term degeneracy.

Ti III $3d^2\,{}^3F \leftarrow 3d^2\,{}^3P,\ 3d4s\,{}^3D$

The species Ti III was chosen for several reasons: (1) there was existing theoretical work,[4] (2) the number of d electrons allows the wave functions to be well correlated without introducing the procedure discussed at the end of Sec. III (which is currently a bit cumbersome to apply), (3) the species is ionized enough to so that $3d$-$4s$ interactions do not need special treatment.

Results for the ${}^3F \leftarrow {}^3P$ transition within the $3d^2$ configuration are given in the first part of Table III. The degree of cancellation with the RHF velocity result is striking; it is $\frac{1}{10}$ of the length result. Yet, FOTOS/$E2$ ("correlated") has corrected them very nicely, so that agreement with the correlated length results is satisfactory. It should be noted that the two length results and Garstang's value[4] agree quite closely. In this case, correlation effects on the length are rather small; as are NON effects (0.04%). Once again, we had a rather large error in ΔE (~0.3 eV), which results in correction factors of 2–3.

For the $3d^2\,{}^3F$ calculation, we included the configurations: $3d^2$, $3s3d^3$, $3dv_g$, $3p^5v_f3d^2$, v_d^2, v_f^2, v_g^2, $3dv_d$, $3p^5v_f3dv_s$, $3p^5v_f3dv_d$, $3p^5v_p3d^2$, $3p^5v_p3dv_d$. Only the first four make large contributions to the (velocity) matrix element. For $3d^2\,{}^3P$ we included: $3d^2$, $3p^5v_f3d^2$, $3s3d^3$, $3s3d^2v_d$, v_d^2, v_p^2, $3dv_d$, $3p^5v_fv_s3d$, $3p^5v_p3d^2$, v_f^2 of which the first four were important for the matrix element. We should note that here we had to remove $3s$ from the "deep core" to produce agreement.

Results for the $3d^2\,{}^3F \leftarrow 3d4s\,{}^3D$ transition are given in the second part of Table III. Here there was very little difference between the length values and only 15% for the velocity values. We may note the considerable difference in the A_Q for these transitions and those within $3d^2$, which is due to the increased ΔE. One might be able to observe the second transition, as it seems moderately large and there are no odd parity states below it. The $M1$ channel will be open of course (J and M_J permitting) due to the configuration mixing of $3d^2$ and $3d\ 4s$.

TABLE III. Spontaneous emission transition probabilities, A_Q, in sec^{-1} for Ti III.[a]

				$3d^2\,{}^3F_J \leftarrow 3d^2\,{}^3P_{J'}$			
			RHF		Correlated		
J	J'	ΔE (eV)	A_Q^L	A_Q^V	A_Q^L	A_Q^V	Garstang[b]
2	0	1.3061	0.0399	0.00423	0.0339	0.0503	0.039
2	1	1.3145	0.0138	0.00144	0.0117	0.0171	0.014
3	1	1.2917	0.0252	0.00273	0.0214	0.0324	0.025
2	2	1.329	0.00124	0.000127	0.00106	0.00151	0.0012
3	2	1.3063	0.00800	0.00085	0.00678	0.0101	0.0079
4	2	1.2767	0.0275	0.00305	0.0233	0.0362	0.027
				$3d^2\,{}^3F_J \rightarrow 3d4s\,{}^3D_{J'}$			
			RHF		Correlated		
2	1	4.7185	34.8	36.8	35.1	43.1	
2	2	4.7352	15.2	16.0	15.3	18.7	
2	3	4.7634	1.12	1.16	1.13	1.36	
3	1	4.6957	17.0	18.1	17.1	21.2	
3	2	4.7124	25.9	27.5	26.2	32.2	
3	3	4.7406	11.4	12.0	11.6	14.0	
4	2	4.6829	10.8	11.6	10.9	13.5	
4	3	4.7111	39.6	42.1	40.0	49.2	

[a] ΔE is the experimental (Ref. 54) energy difference value (no correction for relativity); A_Q^L, A_Q^V are the length and velocity transition probabilities.

[b] The RHF and correlated values agree to the figures published.

Cu II $3d^{10}\,{}^1S \leftarrow 3d^9\,4s\,{}^1D$

We study this transition for reasons similar to those for the Ti III transitions and two additional ones: (1) In calculating the Cu II $3d^{10}\,{}^1S \rightarrow 3d^94p\,{}^1P^0$ electric-dipole transition probability Froese-Fischer[62] apparently found very large deviations from Brillouin's theorem. For example, a multiconfigurational calculation with $3d^{10} + 3d^9v_d({}^1S)$ produced a very large (0.3) coefficient of the second configuration; this is at least an order of magnitude larger than "normal", (2) with so many *d* electrons, NON and correlation effects may be enhanced. Additionally, this line has been seen[63] in the spectra of η Carinae.

To address the first supplemental point, we began by doing a variational CI calculation on $3d^{10} + 3d^9v_d$ for only the v_d radial and the coefficients (the $1s, \ldots, 3d$ radials were from a single configurational RHF calculation on $3d^{10}$). Despite a very careful search, the interaction remained tiny, a result we believe reasonable—for even though 4*s* and 4*d* are nearby, we do have a closed-shell configuration, and Brillouin's theorem is usually good for these. The next step was to look at a three configuration problem, viz: $3d^{10} + 3d^9v_d + 3d^8v_d^2$, all three configurations being among those required by FOTOS/*E*2. Here, we found a large interaction with the last configuration, and a modest one with the middle one. The energy of the combination was much lower than the MCHF (multiconfigurational Hartree-Fock) two configuration energy obtained by Froese-Fischer.[62] The result for the $3d^9v_d$ coefficient, which was maintained in the full FOTOS/*E*2 calculation, does not conflict with Froese-Fischer's,[62] from this point of view: The MCHF calculation allows very great flexibility to the orbitals—as has been pointed out[64] there are essentially as many unknowns as there are mesh points. In this sense we can look at the MCHF calculation as a constrained (by the form assumed for the CI) one involving *n*-tuple excitations of the original RHF orbital, e.g., it contains in a constrained way $3d\rightarrow$, $3d^3\rightarrow$, etc. Additionally $3d^{10}$ is no longer constructed from RHF results to which Brillouin's theorem applies.

The RHF and correlated length and velocity results are shown in Table IV. Correlation has decreased the velocity value by a factor of 2 and brought it into agreement with the length values which changes by 4%. NON effects are small (4%). A rather severe test of FOTOS/*E*2 was involved as the experimental energy difference[54] was 3.256 and the theoretical value 6.783 eV. The large discrepancy arises from the exclusion of $3d^2$ pair excitations from the upper state as our work on $3d \rightarrow 4s$ excitation energies along the entire transition metal period demonstrates[61]—all gaps were accounted for there to 0.1–0.2 eV.

TABLE IV. Spontaneous emission transition probabilities,[a] A_Q, in $\sec^{-1}$ for $\mathrm{Cu}^+\,3d^{10}\,{}^1S \leftarrow 3d^94s\,{}^1D$.

RHF		Correlated		Garstang[b]
A_Q^L	A_Q^V	A_Q^L	A_Q^V	A_Q^L
2.24	3.93	2.33	2.21	2.02

[a] The experimental energy difference (Ref. 54) used was 3.256 eV.

[b] See text for how the results of Ref. 4 were used to produce this "LS" result.

The ${}^1S$ configurations used were: $3d^{10}$, $3d^9v_d$, $3d^8v_d^2$, $3d^8v_s^2$, $3d^8v_sv_d$, and $3d^8v_p^2$, of which only the first two contributed significantly to the quadrupole matrix element. For ${}^1D$, we used $3d^94s$, $3d^9v_g$, $3d^9v_s$, $3d^9v_d$, $3d^9v_g$, $3d^8(v_dv_s + v_dv_g + v_p^2 + v_f^2 + v_d^2)$ of which only the first two contributed substantially to the quadrupole matrix elements.

Garstang's[4] calculation for this line was done on a semiempirical intermediate coupling level. He obtained an A_Q of 1.9 $\sec^{-1}$ for ${}^1S_0 \rightarrow {}^1D_2$ and 0.12 $\sec^{-1}$ for ${}^1S_0 \rightarrow {}^3D_2$. As with electric-dipole transitions there should be an approximate conservation[65] of A_Q, i.e., his *LS* value should be near $1.9 + 0.12 = 2.02$ $\sec^{-1}$. We give this value in Table IV. The value for the second line indicates the ${}^3D_2$ level contains a substantial (~0.2) mixture of ${}^1D_2$ wave function. Given the size of possible *LS* breakdown in these larger species, a mechanism for treating them in an *ab initio* manner will be required. We intend to do this using our recently completed low-*Z*-Pauli general fine structure program[66] which is based on earlier work.[35,67]

At this point some comments on semiempirical methods seem in order. All such methods assume a "model" and use a mixture of experiment and theory to predict the desired result. In the Cu^+ case, for example, a two configuration model $3d^94s + 3d^84s^2$ was assumed, a radial integral $(\int_0^\infty P_{3d}r^2P_{4s}dr)$ extrapolated (value −2.0, *ab initio* result, −2.045), and fine structure constants—needed for off-diagonal matrix elements—extracted from structure information which is primarily diagonal in nature. In addition to the criticisms implicit in the above, the $3d^94s^2$ configuration does not play a dominant role earlier for excitation energies[61] or for transition matrix elements (this work). Yet, despite these remarks, such models seem to work quite well for many transitions. A major cause for this probably is the basic correctness of the independent-particle formalism for these cases.

C. Alkaline earthlike transitions

So far, we have seen that correlation effects can be large for the velocity operator in many circumstances, and as polarizations, for both types of operators. Yet such cases are still apparently amenable to other methods such as the Coulomb approximation and often RHF, as long as they use the length operator.

There are several reasons to expect that this will not be the case for all transitions, however. For example, if we compare $\langle r^2\rangle$ to $\langle r\rangle^2$ we find, in Cs I, the former is only 10–20% larger than the latter. This indicates that the length operator samples a region of configuration space only 10–20% further out than the electric-dipole length operator ($\sim\langle r\rangle$); and for $E1$ there is no question that various kinds of correlation effects can change the value of both length and velocity results (e.g., Ref. 39).

One of the earliest $E1$ correlation mechanisms to be exploited[38,43] involved the $p^2 \leftrightarrow sd$ substitutions for the upper state. These change $E1$ values by factors of 2 (Be–F) (Ref. 38) to 30 (Mg–Cl) (Ref. 43). They also had similar effects (Be–F) on the electronic quadrupole *diagonal* matrix elements.[68] The examples referred to above, involved in-shell substitutions, viz., $np^2 \leftrightarrow nsnd$ or $np^2 \leftrightarrow nsv_d$. Subshell mismatch causes these effects to be damped out. For example in the Cu$^+$ transition, we allowed for $3d4s \leftrightarrow v_p^2$ and $3d^2 \leftrightarrow v_p^2(^1S)$. Both effects were of modest size. They are excluded for the Ti III transition due to total angular momentum restrictions. Contrary to the $E1$ case, however, only one configuration associated with the $p^2 \leftrightarrow sd$ substitution can directly connect with Φ in the transition matrix element. The other configuration will only affect the result either indirectly (e.g., connecting to internal correlation) or by in effect reducing the coefficient of the survivor (renormalization).

The simplest examples of transitions involving in-shell $p^2 \rightarrow sd$ substitutions are the alkaline earthlike *mdns*, $np^2\,{}^1D \rightarrow ns^2\,{}^1S$ ones. These are strong enough to be seen in absorption; in emission the $E1$ process dominates.

C III $2s^2\,{}^1S \leftarrow 2p^2\,{}^1D$, $2d3d\,{}^1D$

We pick an ionized system so that $1s$ may be in the deep core, NON small (<1%), and bivirtual effects depressed. Yet this is still a rather severe test, for the $2s^2 \leftrightarrow 2p^2$ transition is identically zero in the RHF approximation. Upon application of FOTOS/$E2$, the length and velocity results are brought into agreement (Table V), with a tolerably large value of A_Q. The transition from $2s3d$ shows only modest (5–10%) correlation effects, but is so large that it is certainly a candidate for observation in absorption (the equivalent Zn I transition, with smaller A_Q, has been observed[22]).

TABLE V. Spontaneous emission transition probabilities, A_Q, in sec^{-1}.

C III $2s^2\,{}^1S_0 \leftarrow 2p^2\,{}^1D_2$				
RHF			Correlated	
A_Q^L	A_Q^V	ΔE (eV)	A_Q^L	A_Q^V
0	0	18.081	2648	2426

C III $2s^2\,{}^1S_0 \leftarrow 2s3d\,{}^1D_2$			
RHF		Correlated	
A_Q^L	A_Q^V	A_Q^L	A_A^V
0.439×10^6	0.383×10^6	0.370×10^6	0.353×10^6

For the ^1S we used the configurations: $2s^2$, $2p^2$, v_d^2, $2sv_s$, $2pv_p$, v_s^2, v_p^2 and for the ^1D, $2s3d$, $2sv_d$, $2p^2$, v_p^2, $2pv_f$, v_s3d, v_sv_d, v_d^2, $3d^2$, $2pv_p$, v_pv_f, v_f^2, $3dv_d$. Only the first five are important (both terms) for the matrix element. The values for the upper transition ($2s3d$) should be regarded as somewhat tentative, as the upper state was generated from a variational CI calculation in which the lowest root ($2p^2$) was optimized.

Zn I $4s^2\,{}^1S \leftarrow 4s4d\,{}^1D$

The Zn I transition has been observed in absorption by Brown *et al.*[22] The RHF and correlated results are shown in Table VI. While the spread (deviation from the average value) has been reduced from 41% (RHF) to 27% (correlated), the results are not entirely satisfactory. In part, this is due to the failure to remove relativistic effects from the energy difference. A not unreasonable contribution of ~0.2 eV would decrease the spread to 11%, but there is still a significant residual error associated with the transition matrix elements. A much larger spread (factor of 2.3) was obtained by McCavert and Trefftz[18] in their limited MCHF study of BaI $6s^2\,{}^1S \rightarrow 6s5d\,{}^1D$. NON effects are also small (~2%) for this transition. The ^1S was generated with the configurations $4s^2$, $4p^2$, $4sv_s$, $4pv_p$, $3d^94s$ $(4p^2+v_p^2)$, $3d^94s$ $(4pv_p+v_s^2$

TABLE VI. Spontaneous emission transition probabilities,[a] A_Q, in sec^{-1} for Zn I $4s^2\,{}^1S_0 \leftarrow 4s4d\,{}^1D_2$.

RHF		Correlated	
A_Q^L	A_Q^V	A_Q^L	A_Q^V
2592	3932	3604	2744

[a] The experimental (Ref. 54) energy difference, 7.7415 eV, was used here.

$+v_p^2+v_d^2+v_sv_d+v_dv_g$), of which the first seven configurations were important. We should note that the $3d^94s$ $(4pv_p+v_p^2+4p^2)$ configurations were generated from a formally multiconfigurational upper state reference function, i.e., $4p^2$ was added to the reference function (both states). To generate the ^1D wave function, we used

$$
\begin{aligned}
&4s4d,\quad 4p^2,\quad 3d^94d(4p^2+v_p^2)\,,\\
&3d^94d(v_s4d+4sv_d+v_sv_d+v_p^2+v_d^2+4d^2\\
&\qquad +4pv_p+4pv_f+v_pv_f+v_f^2+4dv_d)\,,\\
&3d^94s^24d,\quad 3d^94s4p^2,\quad 3d^94sv_d^2,\quad 3d^94s^2v_s\,,\\
&3d^94s\ (v_s^2+4sv_d+v_sv_d+v_sv_g+4sv_g)\,,
\end{aligned}
$$

of which the first four contributed significantly to the matrix element. We note that for both states, and in fact throughout this work, $3d\rightarrow 4s$, v_s excitations were of little importance. For the ^1D, there were no large polarization ($4s\rightarrow v_s$, $4s\rightarrow v_d$) effects chiefly because the FS radials were generated by a MCHF calculation of $4s4d+4p^2$.

V. DISCUSSION

A major feature of this work was the development of a configuration selection mechanism (FOTOS/$E2$) which yields good transition matrix elements with limited CI. From all indications, this was successful. It is certainly true that some of the FOTOS configurations are extraneous for a given problem. However, we see no need to remove them as computational costs are already low and we do not wish to sacrifice the generality of the approach.

Next, the use of the velocity operator was thoroughly investigated. For transitions within a single configuration, cancellation effects are too large to advise use of the operator. For the other cases, there may be also a moderate preference for the length operator—particularly since independent-particle results with it have on occasion provided answers close (10–20%) to the correlated ones.

We have identified the polarizations $nl\rightarrow v_{l'}$, and $p^2\leftarrow sd$ substitutions as significantly affecting length values. For the latter, if the HF result is zero (e.g., C III $2s^2\rightarrow 2p^2$), the remaining configuration clearly produces striking results, i.e., correlation effects are large. Should the HF result be nonzero (e.g., C III $2s^2\rightarrow 2s3d$), on the other hand, the remaining configuration has only a moderate effect (by lowering the HF coefficient) except for the the few pathological cases where the two configurations are nearly perfectly degenerate. As for other properties, we can expect the more general $l^2\leftarrow(l+1)(l-1)$ substitutions (all FS with the same n) to play a significant role.

While our analysis of NON effects at the RHF level showed they were negligible, past experience[44] demonstrates large NON effects can arise within the correlated parts of matrix elements. The question of whether NON can be completely neglected for the transitions studied here is left open.

Relativistic effects were introduced principally through the energy difference. For Cs I, they were large due to the strong dependence of A_Q in ΔE. Some of this could be removed by use of another quantity such as the oscillator strength which is proportional to $A_Q/(\Delta E)^2$ or by inventing combinations like $(A_V^5/A_L^3)^{1/2}$ which do not depend on ΔE and represent some "average" A_Q [the corresponding $E1$ and f-value quantity is the geometric mean $(f_D^Lf_D^V)^{1/2}$]. Such an expression gives more weight to the velocity than the length value however. Ultimately what is needed is a relativistic-correlation theory. A variant of one is being worked on by the author.

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