Resonance Transition Probabilities for Third-Row Atoms and Ions (Mg I, Si II-III, P II, P IV, S II-III, Cl III) Including the Important Correlation Effects*

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(Received 18 February 1972)

A new atomic structure theory, which includes all the important correlation effects, is used to calculate f values for the transitions $KL\ 3s^a 3p^b 3d^c \rightarrow KL\ 3s^{a'} 3p^{b'} 3d^{c'}$ in the species Mg I, Si II-III, P II, P IV, S II-III, and Cl III. Even for the difficult transitions with $f < 0.1$, the results we report are in good agreement with experiment, in contrast to the order-of-magnitude errors in previously available values. A new type of virtual excitation, from the L shell, is found to contribute 30–60% to such total f values.

An extensive set of nonrelativistic third-row[1] allowed-resonance f values have been calculated and are reported here. All the important correlation effects have been included in both states. These represent the first such calculations in which the new atomic structure theory, which includes electron correlation, is applied to such heavy atoms. The correlation effects to be included are indicated by the theory and are fully taken into account. By contrast, the traditional configuration-interaction (CI) approach is "open ended"; configurations continue to be added, often with little improvement.

Some new effects, not present for second-row[1] atoms, but predicted by the nonclosed many-electron theory (NCMET) of Sinanoğlu,[2] are found to be important for the determination of third-row f values. In particular, it is necessary to allow excitation of electrons from the L shell, something not done in previous calculations on the elements in this row. The present work also indicates how the theory can be applied to even higher-row elements.

It is possible, in an *ab initio* manner, to divide the third-row f values into two classes, $f < 0.1$ and $f > 0.1$. For the first class, the Hartree-Fock and NCMET f values differ by a factor of 10 or more, L-shell excitations contributing 30–60% of the total. For the second class, the Hartree-Fock and NCMET f values usually differ by no more than 50%, and the effect of L-shell excitations is approximately 3%. L-shell contributions remain relatively constant for both classes; strong cancelation effects are responsible for the different roles they play.

Our results, in good agreement with reliable beam-foil measurements, can be used by astrophysicists to determine or revise stellar and solar abundances,[3] collisional excitation rates,[4] etc. The recent availability of rocket-borne spectrographs,[3] which opens up the resonance wavelength region, and the sensitivity of the curve of growth[3] to the smaller f values, mean that resonance f values will play an increasing role in abundance determinations. Because silicon and magnesium are the dominant contributors of electrons in solar-type stars, continuous opacity and model atmospheres depend heavily on their abundances.[5]

The agreement between our nonrelativistic NCMET and experiment suggests that relativistic contributions to third-row f values, for L-S-coupled states, are smaller than correlation effects. Similarly, relativistic contributions to *excitation* energies are smaller than correlation contributions in the third-row elements.[6]

To apply the theory to third-row KLM configurations, the restricted Hartree-Fock (HF) function Φ_{RHF} is used as a starting point, the "Hartree-Fock sea"[2] consisting of all $1s$, $2s$, $2p$, $3s$, $3p$, and $3d$ spin orbitals. For the second row, only $1s$, $2s$, and $2p$ were included in the "sea."[7]

The correlation function is rigorously divided into three nearly independent parts.[2,6,7] The all-external part χ_U by hypothesis does not affect f values, because it has little effect on the charge density, and so can be neglected. This has been confirmed by Westhaus and Sinanoğlu for the second row[8] and here for the third row.

The internal part of the correlation function, χ_{INT}, consists of all determinants which can be formed from just the "Hartree-Fock sea" spin orbitals, consistent with parity and symmetry. The unknowns, finite in number, are the coefficients of the determinants.

The semi-internal and polarization correlation function χ_F mainly consists of all determinants formed from $N-1$ (there are N electrons) "HF sea" spin orbitals and one "semi-internal" spin orbital, consistent with symmetry and parity. "Semi-internal" orbitals, $\hat{f}_{ij;k}(\vec{r})$, are functions "outside the HF sea," i.e., $\langle \hat{f}_{ij;k}(\vec{r}), m \rangle = 0$ for

TABLE I. Resonance multiplet absorption oscillator strengths for atoms and ions of the third row.[a]

WAVE-LENGTH (Å)	TRANSITION	f^{RHF}	f^{NBS}	f^{NCMET} (This work)	f^{EXPT}
		$f < 0.1$			
1814	Si II $3p\ {}^2P^0 \rightarrow 3p^2\ {}^2D$	.454 .504	.0064	.0137 .0269 (.0192)	
1308	P II $3p^2\ {}^3P \rightarrow 3p^3\ {}^3P^0$	.292 .256		.0382 .0436 (.0408)	.029±.002 [b] .040±.006 [c]
1198	S III $3p^2\ {}^3P \rightarrow 3p^3\ {}^3D^0$	.389 .458	.62	.0358 .0450 (.0401)	.022±.001 [d]
1011	Cl III $3p^3\ {}^4S^0 \rightarrow 3p^4\ {}^4P$	.685 .777	1.2	.0855 .1032 (.0939)	.043±.003 [e]
	S II $3p^3\ {}^2D^0 \rightarrow 3p^4\ {}^2D$	.394 [f]		.0494 [f]	
		$f > 0.1$			
2780	Mg I $3p\ {}^3P^0 \rightarrow 3p^2\ {}^3P$	.804 .504	.61	.639 .604 (.621)	.50±.05 [g] .53±.05 [h]
1299	Si III $3p\ {}^3P^0 \rightarrow 3p^2\ {}^3P$	.651 .468	.564	.543 .569 (.556)	.74±.17 [i]
826	P IV $3p\ {}^3P^0 \rightarrow 3d\ {}^3D$	.891 .777	.796	.789 .805 (.797)	.47±.07 [b,j]
1196	Si II $3p\ {}^2P^0 \rightarrow 3p^2\ {}^2P$	1.248 .614	.91	.878 .864 (.871)	

[a] The restricted Hartree-Fock values, computed by the authors, are given in column 3; the dipole length (f_R) result is the upper, and the velocity (f_∇) result is the lower quantity. In column 4, we give the values reported in Ref. 12; these are purely theoretical. In column 5, the results of this work, based on the new atomic structure theory of Sinanoğlu (Ref. 2), which includes electron correlation, are given. The length result is first, the velocity result second, and the geometric mean of the first two, last. All experimental measurements (column 6) were made by the beam-foil method except those of Ref. 14 which used the phase-shift method.

[b] Ref. 13.

[c] Ref. 14.

[d] Ref. 15.

[e] Ref. 16.

[f] Since the upper term has not been observed and all-external energies (see text) are not yet available, the wavelength is unknown. Hence, only the geometric mean is presented.

[g] Ref. 17.

[h] Ref. 18.

[i] Ref. 19.

[j] Ref. 20.

$\{m \in$ "HF sea"$\}$. As NCMET shows, the symmetry of the angular parts, spherical harmonics, is ≤ 6 in the third row,[6] whereas it is ≤ 3 in the second row.[2,7] Each of these spherical harmonics is multiplied by a "semi-internal" radial function $f_{ij;k}{}^{l}(\vec{r})$. These are determined variationally.

Strictly, each semi-internal configuration has a unique radial function, with different radials for different parents as well. In the second row, good results[7,8] were achieved by taking all radials of the same symmetry equal. In the third row, at the minimum, a different set of radials for L and M excitations must be used.[6] Even though K-shell excitations may be excluded because of their small size,[6-8] we have 1–5000 linear unknowns (coefficients) and 14 nonlinear unknowns (radial functions).

Solution of this problem is computationally quite unfeasible. However, approximations of NCMET show[9] that χ_F can be divided into several nearly independent parts. In practice,[6] each part has fewer than 750 determinants and *four* nonlinear unknowns. Moreover, each configuration has a unique radial, the only radial approximation being that all parents belonging to the same configuration have equal radials.

Through the use of efficient computational algorithms, *complete* correlation functions are obtained in 10–20 min on a CDC 6600, separately optimizing each radial. The radials are found to vary widely. Finally, all individual correlation functions are allowed to simultaneously interact as units. This accounts for much of the small residual error made in assuming complete independence of the parts.[6]

Formulas giving the length (R) and velocity (∇) expressions for the f values are given elsewhere.[8] In their evaluation, the nonorthogonality of the spin orbitals must be taken into account. This is particularly essential for neutral and lightly ionized species in which the configurations $KL\ 3s^a 3p^b 3d^c$ and $KL\ 3s^{a+1} 3p^{b-2} 3d^{c+1}$ both appear (one in Φ_{RHF} and one in χ_{INT}). Nonorthogonality effects can account for 10% of these f values. (For such species, NCMET f values may differ by an order of magnitude or more over RHF f values.) Similar effects have been noted in the second-row elements[10,11]; these generally are smaller because the d radial is a "semi-internal" one.

The exact nonorthogonality procedure is used to evaluate $\langle \Phi_{\mathrm{RHF}} | D | \Phi_{\mathrm{RHF}}' \rangle$, $\langle \Phi_{\mathrm{RHF}} | D | \chi_{\mathrm{INT}} + \chi_F' \rangle$, and $\langle \chi_{\mathrm{INT}} + \chi_F | D | \Phi_{\mathrm{RHF}}' \rangle$, where D is the dipole operator. These are the principal contributors to the f value.

A more efficient, but slightly approximate, nonorthogonality procedure is used[6] to evaluate the remaining term, whose contribution to f is ≤ 0.001, and computation times are reduced to 5 min.

In evaluating f values, the exact nonrelativistic excitation energy should be used. This is the sum of the HF, internal, semi-internal, and all external excitation energies.[2,7] Since third-row relativistic HF results are unavailable, the nonrelativistic excitation energy cannot be extracted from the experimental value. We have used this last quantity to evaluate the length (f_R) and velocity (f_∇) operator forms for the NCMET and RHF f values. Typically, excitation energies are about 0.01 a.u. too large, thus making f_R too large and f_∇ too small. This can account for part of the small difference between the f_R and f_∇ values. However, the best form of f to be used (when f_R and f_∇ are quite close) is the geometric mean in which the excitation energy cancels out and makes the final f values even more accurate.

In Table I, the new NCMET results are compared with existing[12-19] results. Three f values, not yet measured, are predicted by NCMET. The NCMET results are in good agreement with experiment, even for the difficult $f < 0.1$ transitions, in contrast to the order-of-magnitude difference of the RHF and National Bureau of Standards (NBS) results. For P II, NCMET clearly favors one experimental value over the other. The NCMET 1814-Å Si II f value can be used to revise collisional excitation rates.[4]

For the remaining transitions in Table I, correlation effects are small, and the f value is fairly well approximated by the RHF result. Consequently, the NBS values may be more reliable in these cases, although the most accurate values are still given by NCMET.[2] The NCMET result for the 826-Å P IV transition suggests that a new experimental determination may be worthwhile.[20]

Finally, our results are particularly timely. Much beam-foil work has begun to center on the third-row elements within the past year.[13,16,19]

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*Work supported by a grant from the National Science Foundation.

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Alternative Decay Channels of a CO^- Feshbach Resonance*

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(Received 27 December 1971)

By means of on- and off-resonance energy-loss measurements, we have observed the decay of the 10.04-eV resonance in CO to the $A\,^1\Pi$, $a\,^3\Pi$, and $a'\,^3\Sigma^+$ states. The measurements identify the resonance as a $^2\Sigma^+$ state of CO^-.

A resonance in scattering of electrons on CO has been discovered by Sanche and Schulz[1a] in transmission at ≈10.04 eV. Subsequent work has indicated that the resonance is observable and approximately isotropic in both elastic scattering[1b-3] and in inelastic excitation of the $v'=1$ vibrational level of the ground electronic state.[3] The purpose of this Letter is to report experimental observations of decay of this resonance into a number of vibrational levels of at least three different electronically excited states. These observations were made by two different experimental techniques, i.e., (a) by obtaining excitation functions for individual vibrational levels and (b) by observing the energy-loss spectra both on and off resonance. The information obtained in these measurements provides (a) a definitive classification of the resonance and (b) direct experimental evidence of configuration interaction occurring between electronic states which comprise the $a'\,^3\Sigma^+$ decay channel and the $b\,^3\Sigma^+$ parent Rydberg state.

The instrument used in these measurements was a hemispherical electron monochromator analyzer using copper hemispheres of 5.08 cm (2 in.) mean radius as the energy dispersing elements. The target gas cell was a molybdenum cylinder 1.27 cm (0.5 in.) in diameter, with an entrance aperture of 0.165 cm diam (0.065 in.) and 0.063-cm-diam (0.025-in.) exit apertures at $\theta = 0°$, 30°, 45°, and 90°. The gas pressure inside the cell was about 0.02 Torr, and about 1000 times less than that in the surrounding vacuum chamber. The entire monochromator section can be rotated about the scattering center in fixed angular steps of 5° from 0° to 100°. The scattered electrons are energy analyzed in the analyzer hemisphere and counted by an eighteen stage Be-Cu multiplier. Output pulses produced by the individual electrons are transmitted down a 50-Ω line to a fast counting chain and can be counted on a scaler and stored in an on-line computer or displayed on a count-rate meter connected to an X-Y recorder.

Figure 1 shows excitation functions corresponding to the $v'=2$, 3, and 4 levels of the $A\,^1\Pi$ state of CO along with a background trace taken at 8.45-eV excitation energy. These excitation functions as well as all other data reported here were obtained at a scattering angle of 45° with an instrumental resolution of less than 50 meV full width at half-maximum. The data in Fig. 1 do not represent "pure" excitation of the indicated