CONF-890387--1

UCRL- 100712
PREPRINT



# Semiclassical Matrix-Elements of High-Charge Ions

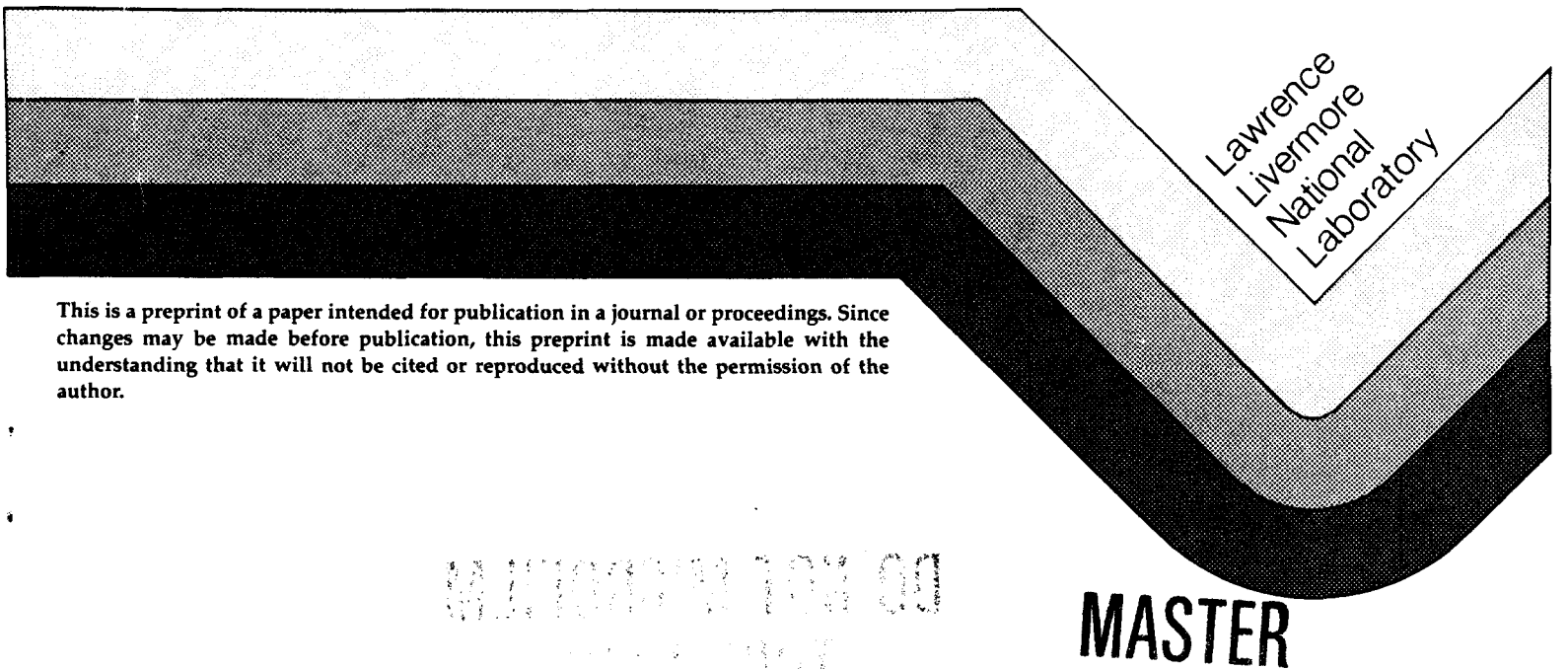
Richard M. More

This Paper was Prepared for Submittal to

Workshop on Highly Charged Ions
New Physics and Advanced Techniques

Lawrence Berkeley Laboratory
Berkeley, California

March 13-15, 1989



---

UCRL--100712

DE89 009258

# SEMICLASSICAL MATRIX-ELEMENTS OF HIGH-CHARGE IONS

Richard M. More

Lawrence Livermore National Laboratory

University of California

Livermore, CA 94550

## ABSTRACT

We apply a new semiclassical method to study radiative transitions of high-charge ions. One-electron matrix-elements calculated with WKB wavefunctions are compared with self-consistent field calculations for molybdenum at various stages of ionization. The WKB method is able to follow the (large) changes in the 1s → np matrix-elements produced by ionization.

More and Warren recently discovered a method to calculate matrix elements for electronic transitions using semiclassical (WKB) wave-functions.[1] Typically the accuracy is ≃ 10% for all matrix-elements, although there are a few exceptions. The method is simple and works for many non-relativistic quantum systems. This brief report will describe a first application to one-electron radiative matrix-elements for high-charge ions.

In brief, the method is based on the WKB travelling waves.

$$\Psi_{n\ell}^{(\pm)}(r) = \frac{C_{n\ell}}{\sqrt{q(r)}} \exp \pm i[\int q(r')\, dr' - \pi/4] \tag{1}$$

where $q(r) = (2m/\hbar^2)^{1/2}\, [E_{n\ell} + eV(r) - \hbar^2/2m\, (\ell + 1/2)^2/r^2]^{1/2}$ is the radial wave-vector (= $m/\hbar$ times the radial velocity). $V(r)$ is the self-consistent potential.

The wave-functions are normalized by

$$\frac{1}{2}\, \mathrm{Re} \int \Psi_{n\ell}^{(+)}(r)\, \Psi_{n\ell}^{(-)}(r)\, dr = 1 \tag{2}$$

and the dipole matrix-element is calculated by a saddle-point method as follows:

$$\begin{aligned} R_{n\ell}^{n'\ell'} &= \frac{1}{2}\, \mathrm{Re} \int \Psi_{n\ell}^{(+)}(r)\, r\, \Psi_{n'\ell'}^{(-)}(r)\, dr \\ &= \frac{1}{2}\, \mathrm{Re} \int e^{ig(r)}\, dr \\ &\simeq \frac{1}{2}\, \mathrm{Re} \left[ \Psi_{n\ell}^{(+)}(r_s)\, r_s\, \Psi_{n'\ell'}^{(-)}(r_s) \sqrt{\frac{2\pi i}{g''(r_s)}} \right] \end{aligned} \tag{3}$$

where the saddle-point $r_s$ is defined by requiring $g'(r_s) = 0$. The saddle-point is a complex number but with Eq. (1) there is no difficulty calculating the wave-functions at complex radii, assuming the potential is known. For

hydrogenic ions, $V(r) = Ze/r$ is analytic except at the origin, and there is no problem.

We have compared Eq. (3) with exact quantum results for dipole and quadrupole line transitions of hydrogenic ions, and also for the photoelectric transitions, and have compared to numerical results for line transitions in a Debye-screened Coulomb potential, a simple model for an ion in a plasma. We have also made comparisons for matrix-elements of spherical harmonic functions and for the one-dimensional harmonic oscillator. To date the method succeeds for everything.

By this we mean that it predicts matrix-elements to about 10% accuracy (over a range of three or four orders of magnitude in the matrix-element) and does this without modification to the basic formula. Thus the method is robust and reliable.

To compare with quantum wave-fuctions we form

$$\Psi_{n\ell}(r) = \frac{1}{2}\,\mathrm{Re}\left[\Psi^{(+)}_{n\ell}(r) + \Psi^{(-)}_{n\ell}(r)\right] \tag{4}$$

In this equation, the instruction to take the real part replaces the usual "connection formula" of the WKB theory, and gives a well behaved wave-function which correctly decreases at large and small r. The numerical values are very accurate except close to the turning-points of the classical motion, where $q(r) = 0$; at these points the WKB functions have weak singularities.

Good agreement with quantum wave-functions is obtained despite the unusual normalization rule of Eq. (2) and would not be found if one attempted to force the customary quantum normalization upon the WKB wave-function. We have discovered evidence that this reflects a more fundamental semiclassical structure; we find (numerically) that our wave-functions satisfy a one-sided orthonormality condition.

$$\frac{1}{2}\,\mathrm{Re}\int \Psi^{(-)}_{n\ell}(r)\,\Psi^{(+)}_{n'\ell'}(r)\,dr \tilde{=} \delta_{nn'} \qquad (n' \geq n) \tag{5}$$

This relation applies for both Coulomb and screened-Coulomb cases, as well as for other cases mentioned above. The diagonal terms (n = n') are obviously unity as a consequence of Eq. (2) but the fact that the off-diagonal terms are small ($\sim 10^{-3}$) points to something new and remarkable in the semiclassical theory.

Equation (3) for the matrix-element gives a nearly closed-form expression for $R^{n'\ell'}_{n\ell}$, which is very useful in attempting to see more clearly into the physics. We have discovered that the magnitude of the saddle-point $r_s$ is nearly equal to the radius of second-order orbit-intersection, which is given for hydrogenic transitions $n, \ell \to n, \ell + 1$ by

$$r_i = \frac{4(\ell + 1)}{\left(\frac{\ell + 3/2}{n}\right)^2 - \left(\frac{\ell + 1/2}{n}\right)^2} \frac{a_o}{Z} \tag{6}$$

This leads to a simple intuitive picture for the matrix-element, in which the radiative transition is seen as a <u>quantum jump</u> from initial to final orbit occurring during the second-order orbit intersection.

The picture gives a number of useful insights. For example, the matrix-element is typically larger with better orbit contact, a consequence of the factor $1/\sqrt{g''(r_s)}$ in Eq. (3). We find that the matrix-element is very small for transitions such as $2p \to 3s$ which do not have second-order orbit-intersection.

For application to high-charge ions it is necessary to know the atomic self-consistent potential as a function of a complex radius in order to search for the saddle-point of Eq. (3). We make the assumption that the potential is generated by a charge-density of the form

TABLE 1

Hydrogenic Matrix-Elements

(atomic units)

| Transition | WKB R(n, l, n', l') | Exact R | Percentage Difference |
|---|---|---|---|
| 1s - 2p | 1.2510 | 1.2903 | 3.04 |
| 1s - 3p | 0.4782 | 0.5167 | 7.45 |
| 1s - 4p | 0.2796 | 0.3046 | 8.21 |
| 1s - 5p | 0.1910 | 0.2087 | 8.49 |
| 2s - 3p | 3.1439 | 3.0648 | 2.58 |
| 2p - 3d | 4.6123 | 4.7480 | 2.86 |
| 2p - 3s | 1.0019 | 0.9384 | 6.76 |
| 3s - 4p | 5.7413 | 5.4693 | 4.97 |
| 3p - 4d | 7.6298 | 7.5654 | 0.85 |
| 3p - 4s | 2.6982 | 2.4435 | 10.42 |
| 3d - 4f | 9.9253 | 10.2303 | 2.98 |
| 3d - 4p | 1.4379 | 1.3023 | 10.41 |

$$\rho(r) = Ze\,\delta(\vec{r}) - \sum_n P_n A_n^2 r^{2(n-l)} e^{-2\alpha_n r} \qquad (7)$$

Equation (7) gives the charge density resulting from hydrogenic wave functions for states of angular momentum $\ell = n - l$ (e.g., 2p, 3d, 4f, ...). $P_n$ is the number of electrons in shell n in the ground state ion. The parameters $\alpha_n$ must be chosen to represent the charge density in the ion in question; $A_n$ is determined by normalization to be

$$A_n^2 = \frac{(2\alpha_n)^{2n+1}}{4\pi(2n)!}$$

This charge density is easily integrated to give an analytic representation of the potential, a form introduced by Klapisch under the name parametric potential.[2]

For our evaluations we determined the parameters $\alpha_n$ by use of effective charges supplied by a screened-hydrogenic code.[3] The results of this procedure are neither self-consistent, relativistic nor terribly accurate. A much better calculation could easily be done.

However the results are good enough to show that the WKB method is able to reproduce the large systematic changes in oscillator-strengths with ionization.

For transitions $1s \rightarrow np$ we have found that the saddle-points are nearly independent of the ion charge-state Q (especially for $n = 4.5$), even though the oscillator-strength changes by a large factor $\simeq 5$ due to variations in the screening. We are able to unambiguously attribute the majority of this large change to altered normalization of the upper-state wave-function: in the less-ionized ions the upper level experiences a more strongly screened potential, relaxes outward, and has reduced overlap with the K-shell wave-function as measured by the product in Eq. (3).

ACKNOWLEDGMENT

The numerical data reported in this paper were produced with the assistance of K. H. Warren of the Lawrence Livermore National Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

## REFERENCES


1. R. M. More and K. H. Warren, J. Phys. France 50, 35 (1989).
2. M. Klapisch, Comp. Phys. Comm. 2, 269 (1971).
3. R. M. More, J.Q.S.R.T. 27, 345 (1982).

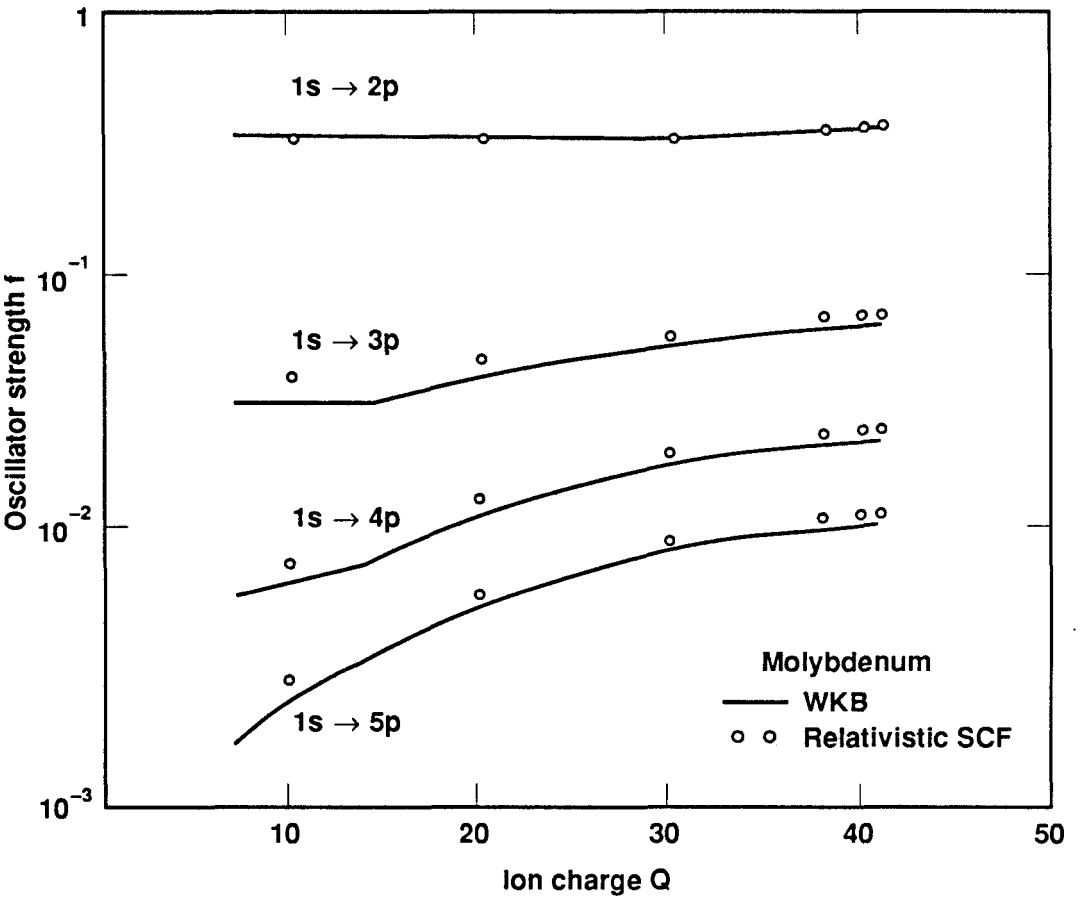



Figure 1. Oscillator-strength for transitions 1s → np of Molybdenum ions calculated by the method of Eq. (3). The comparison data was provided by D. A. Liberman and is obtained from a relativistic self-consistent field calculation.