

Theoretical Calculations of the Threshold Energy (∆E In EV) of the Inner Shell Excitation in Be+ Ion

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ABSTRACT

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In this paper, we have carried out theoretical calculations of the threshold energy (ΔE in eV) of the inner-shell excitation, which leads to autoionization, 1s2 2s 2Se \rightarrow 1s 2s2 2Se optically forbidden transition in Be+ ion employing the configuration interaction wave functions for both the initial and final states involved in the transition matrix elements.

Keywords : CI Configuration, Hartee- Fock, Optical Strength

I. INTRODUCTION

There are many methods to calculate the oscillator strengths. Absorption optical oscillator strength for atoms molecules and ions in the discrete and continuum regions provide some valuable quantitative information for further understanding the electronic structure of matter and its interaction with electromagnetic radiation. This information is of importance in the fields of application such as biophysics, testing and development of theoretical methods, Lithography, aeronomy, health physics, radiation protection, astrophysics, atmospheric physics, laser physics, radiation physics, plasma physics, gas discharge, mass spectroscopy, space research, fashion research physics, etc. The oscillator strengths and cross-section provide an appropriate test from atomic structure calculation, quantative results of oscillator strengths and cross-section are

also crucial requirements for the development and evaluation of quantum mechanical theoretical methods and the modeling produced used for the various phenomena involving electronic transitions induced energetic radiations.

After the beginning of computational quantum chemistry¹⁻¹⁰, the description of electronic structure based on the Hartree Fock (HF) approximation still forms the basis of most theoretical approaches. The number of problems that one may solve performing Hartree-Fock calculations is rather limited. Excited states, transition states, and many atomic, molecular, and ionic properties are not adequately described by a single-determinant Hartree-Fock function. Even ground states of atoms and molecules may require Hartree-Fock treatment not only for a quantitative but sometimes even for a qualitatively correct description. For such hard cases, the concept of correlation energy, defined as the difference between

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the exact energy from the non-relativistic Shroedinger equation and the Hartree-Fock energy, is not useful because the single determinant HF model is no longer adequate as the zeroth-order solution. Despite great efforts to develop the many-body theory, configuration-interaction (CI) is the most frequently used for Hartree-Fock calculations. We have also performed theoretical calculations of the threshold energy and dimensionless absorption optical oscillator strengths (OOS), of both the length and velocity forms (fL and fv respectively), for the electric dipole-allowed resonance excitation in the same ions as mentioned above using the configuration interaction wave functions for the ${}^{2}S^{e}$ and ${}^{2}P^{0}$ states involved in the transition matrix elements.

II. HAMILTONIAN MATRIX ELEMENT

In CI wave functions one of the important stages is the construction of the Hamiltonian matrix. In general, we can write the Hamiltonian matrix in the CI wave function

$H_{ij} = \langle \Phi_i H \Phi_j \rangle$	
or, $Hij = \langle \Phi_i H_0 + V \Phi_j \rangle$	(1)
where in atomic units	
$H_0 = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right)$	
and, $V = \sum_{i < j} \frac{1}{r_{ij}}$	(2)
Then	
$\langle \Phi : H_{c} \Phi : \rangle = \sum \chi(\sigma, \sigma) \langle P_{c} \rangle \left[-\frac{1}{2} \frac{d^{2}}{d^{2}} - \frac{z}{d^{2}} + \frac{l_{\sigma}(l_{\sigma}+1)}{d^{2}} \right] P_{c} \rangle \delta_{l} \rangle$	(3)

$$\langle \Phi_{i} | H_{0} | \Phi_{j} \rangle = \sum_{\sigma \sigma} \chi(\sigma, \sigma) \langle P_{n_{\sigma}l_{\sigma}} | -\frac{1}{2} \frac{\alpha}{dr^{2}} - \frac{1}{r} + \frac{1}{2r^{2}} | P_{n_{\sigma}l_{\sigma}} \rangle. \delta_{l_{\sigma}l_{\sigma}}$$
(3)

$$\langle \Phi_{i} | V | \Phi_{j} \rangle = \sum_{\rho, \sigma, \rho', \sigma', k} [y(\rho, \sigma, \rho', \sigma', k)^{2} R^{k} (n_{\rho}l_{p}, n_{\sigma}l_{\sigma}; n_{\rho}l_{p}, n_{\sigma}l_{\sigma})]$$
(4)

We recall that, for non-zero {y}, ϕ_i and ϕ_j must have at least (N-2) orbitals in common, and the possible choices of ρ , ρ' , σ' are determined as follows: -

(i) if Φ_i and Φ_j ; have exactly (N - 2) orbitals in common, then p,σ are subsells (possibly with $\rho = \sigma$) in Φ_i which contain the two remaining electrons, while ρ', σ' are the subshells in Φ_j which contain the two different electrons.

(ii) if Φ_i and Φ_j ; have (N-1) orbitals in common, then ρ (or σ , so that $\rho < \sigma$) is the subshell of Φ_i containing the remaining electron; ρ' is similarly defined with respect to Φ_j ; and $\sigma = \sigma'$ can be any subshell occupied by one or more of the (N - 1) common orbitals.

(iii) if F_i and F_j are built from the same N electrons, then $(\rho, \sigma) \equiv (\rho', \sigma')$ can be any pair of subshells, with $\rho = \sigma$ allowed if there are two or more in the corresponding subshells.

III.ONE ELECTRON SYSTEM

For non-zero {x}, Φ_i and Φ_j must have at least (N-1) orbitals in common and the possible choices of σ , σ' are determined as follows:

(i) If Φ_i and Φ_j have exactly (N-1) orbitals in common then σ is the subshell in Φ_i which contains the remaining electron, while σ' is similarly defined with respect to Φ_j .

(ii) If Φ_i and Φ_j are constructed from the same N orbitals, then these two electrons must be identical (including their coupling schemes) for a non-zero matrix element. In this case, $\sigma = \sigma'$ and the summation in (3) runs over all occupied subshells, with $\alpha(\sigma,\sigma')$ equal to the number of electrons in subshells σ .

IV. RADIAL FUNCTIONS

The radial functions as linear combinations of Slater-type orbitals, following Clementi and Roetti¹²

$$P_{nl}(r) = \sum_{i=1}^{K} C_{inl} r_{inl}^{I} \exp\left(-\xi_{inl} r\right), n > 1$$

To maintain orthonormality amongst the one-electron orbitals it is necessary to choose

 $\int_{0}^{\infty} P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'}, \quad 1 + 1 \le n' < n$

If k = n - 1 then the coefficients $\{c_{jnl}\}$ are uniquely determined by the conditions (6), for a given choice of $\{I_{jnl}, \xi_{jnl}\}$. If K > n-1. Most of the coefficients can be treated as variational parameters, either in HF or SOC calculations. Orbitals involved in the ground state configuration are given in the Clementi and Roetti tables¹². Excited orbitals are not available. So one must have to generate excited orbitals for the Cl calculation.

V. GENERATION OF EXCITED ORBITALS BY OPTIMIZATION PROCESSES

The computer program of Hibbert CIV3¹³ has incorporated two optimization routines, either or both of which may be used.

Firstly VA04A, which is based on the direct search method of Powell. In this scheme, searches are made along each of n (number of variables) directions which are initially chosen as the co-ordinate axes and are subsequently updated, so that, if the function being minimized is a quadratic form these directions are mutually conjugate concerning the matrix of coefficients of the second-degree terms.

Secondly, MODDAY, which is based on Fletcher and Powell's modification of Davidson's scheme, explicitly uses the gradient of the function. If the function can be expressed as a quadratic form, then the displacement between the point x and the minimum x_0 is

 $\mathbf{x}_0 - \mathbf{x} = -\mathbf{G}^{-1}\mathbf{g}$

(7)

(5)

(6)

where g is the gradient at x (ie. $g_i = \partial f/\partial x_i$) and G is the matrix of the second derivatives $(G_{ij} = \partial^2 f/\partial x_i \partial x_j)$. In practice G^{-1} is not calculated, but is the limit of a sequence of matrices H produced by iteration. $H^{(i+1)}$ is obtained from $H^{(i)}$ by using information gained by moving down the directions $S^{(i)} = -H^{(i)}g^{(i)}$. Here $H^{(0)}$ is taken as steepest descent scheme.

Using these radial functions one can then evaluate the radial intergrals in (3) and (4), and hence the Hamiltonian matrix can be constructed.

VI. OSCILLATOR STRENGTHS AND TRANSITION PROBABILITIES

If one can determine the wavefunctions of the form (1) in this way, they can be used to obtain optical oscillator strengths, in length (f_L) and velocity (f_v) form, for transition between initial and final states $\Psi^{(i)}$ and $\Psi^{(f)}$ with energies $E^{(i)}$ and $E^{(f)}$ respectively.

$$f_{L} = \frac{2\Delta E}{3g_{i}} | \langle \Psi^{(i)} | \sum_{p=1}^{N} r_{p} | \Psi^{(f)} \rangle |^{2}$$
and
$$f_{v} = \frac{2}{3g_{i}\Delta E} | \langle \Psi^{(i)} | \sum_{p=1}^{N} \nabla_{p} | \Psi^{(f)} \rangle |^{2}$$

$$=$$

$$(8)$$

where $\Delta E = E^{(f)} - E^{(i)}$ and $g_i (2L_i + 1) (2S_i + 1)$ is the statistical weight of the lower state $\Psi^{(i)}$. For the exact wavefunctions, equations (2.13) and (2.14) give identical results. For approximate wavefunctions, the two equations may yield different results. The reliability of either depends not only on the closeness of the two values but also on their stability as more configurations are added. Such convergence may be more quickly achieved in one form of the oscillator strength than in the other.

Parameters for the bound orbitals used in the present calculation for Be⁺ are shown in Table 1 and the numbers below the configurations give their weights are also given in Table 2 and 3.

VII. RESULTS AND DISCUSSION



Table 2 displays our present non-relativistic theoretical excitation threshold (ΔE in eV) of the lowest-lying autoionization level generated due to the inner-shell optically forbidden excitation $1s^2 2s 2s^e \rightarrow 1s 2s^2 2S^e$ transition in Be⁺ obtained using the configuration interaction wave functions for both the initial and final states involved in the transition matrix elements. Table 2 also exhibits the excitation energy and the optical oscillator strengths, of both the length and velocity forms (f_L and f_v respectively), for the optically allowed excitation $1s^2$ $2s^2s^e \rightarrow 1s^2 2p 2P^0$ resonance transition employing the configuration interaction wave functions for both $2S^e$ and $2P^0$ states. For the physically meaningful comparison, we have also presented other available relevant theoretical results (In the case of C³⁺) in the same table.

So many features emerge from Table 2 also. In the case of the inner-shell excitation $1s^2 2s 2S^e \rightarrow 1s 2s 2S^0$ optically forbid- den transition, which leads to autoionization, we have compared our excitation threshold energy with the result of P. Kumar for C^{3+} better agreement with the other theoretical result. Finally, for Be⁺, the situation is similar to C^{3+} . In general, our present theoretical result tends to lie in a similar trend to the other theoretical result in Be⁺ ions of present consideration.

As far as outer shell excitation is concerned $(1s^2 2s {}^{2}S^{e} \rightarrow 1s^{2} 2p {}^{2}P^{0})$ we have compared our theoretical excitation threshold energy and optical oscillator strengths, of both the length (fL) and velocity (fv) forms, with the experiment of martin and wiese¹⁴ and Anderson et al¹⁵. There is good agreement between the length and velocity forms of the oscillator strengths. For Be⁺, other theoretical predictions as well as experimental observations are not available. However, there is reasonably good agreement between the length and velocity forms of the oscillator strengths. As we have compared with C3+, our theoretical transition energy and oscillator strength are in good agreement with the experimental result of Martin and Wiese.¹⁴

In general, the excitation energy for both the inner shell and outer shell is in good agreement with the experiment and other theories and excitation energy increases with the increase of atomic number (Z) in all ions of present consideration in the Be⁺ which is general behavior. In the case of the velocity forms of oscillator strength and also with other available theoretical predictions and experimental observations. It is also clear from the table that the value of the velocity form is larger than the length form in the case of Be⁺ ionic system.

VIII. CONCLUSION

Our present non-relativistic theoretical investigation, of the excitation energy and oscillator strengths, demonstrates that another theoretical description (C^{3+}) is not so adequate whereas the configuration interaction calculation is capable of yielding good results for both the inner-shell excitation which leads to autoionization as well as the outer-shell excitation in the lowly ionized atoms of the lithium isoelectronic sequence. However, there is disagreement between our elaborate theoretical calculation and experimental measurement. This may be probably due to neglect of the relativistic effect, polarization effect, and quantum electrodynamic effect in our present calculations. The present configuration interaction wave functions may be of use for accurate calculations of the cross sections, which are very sensitive to the wave functions, by photon and electron impact.

Orbitals	Clementi-Type	Slater-type	Power of r	Exponent
	coefficient			
1s	0.8967507	6.9868046	1	2.4758305
	0.1122409	2.2795898	1	4.6894199
	-0.0008000	-0.0003506	2	0.7650009
	0.0076480	0.0358987	2	1.7530008
	0.0008800	0.0003166	2	0.6271107
2s	-0.1450009	-1.1297436	1	2.4758309
	-0.0157508	-03198848	1	4.6894198
	0.4167908	0.2463434	2	0.7658000
	-0.0798106	-0.3749576	2	1.7530008
	0.6461288	0.2323538	2	0.6271107
3s	0.0943088	0.6558708	1	2.2952988
	-0.9218218	-0.2119088	2	0.5243357
	1.4915829	0.0248485	3	0.3972204
4s	0.4579188	2.5948077	1	2.0023098
	-1.6782485	-1.9436982	2	1.0011987
	1.4446572	0.3337825	3	0.8421009
	-0.6948590	-0.0000602	4	0.2103089
2p	1.0000000	0.2327980	2	0.5269990
3p	0.8163758	-0.0106379	3	0.3195980
	-1.3672295			
4p	1.1053763	0.0927238	2	0.3503346
	-2.2352896	-0.0169656	3	0.3173318
	1.7534148	0.0002748	4	0.2298383
3d	0.9999999	0.0090088	3	0.3332469
4d	1.5217852	0.0069884	3	0.2748498
	-2.0069476	-0.0004187	4	0.2462568
4f	0.9999988	0.0003996	4	0.2789989

Table 1: Parameters for the bound orbitals used in the present calculation for Be⁺

Table-2: Configuration used for ground state in the present calculation for Be⁺ The numbers below the configuration give their weights

2Se	1s4P ²	1s4f ²	1s4d ²	1s3p (³ P)4p	1s 3p (¹ p)	1s3p2	1s3d (3D)	1s3d(1D)4d
					4p		4d	
1s2s(1S)3s	-0.0066088	0.01428343	-	0.02923496	0.02923496	0.02702462	0.00299813	0.00237799
			0.00894694					
1s2s(3S)3s	0.01264039	-	0.01667738	-	-	-	-	-
		0.02665614		0.05450693	0.00122120	0.05187234	0.00587511	0.00138360
1s2s(1S)4s	-	-	-	0.01715922	0.00405439	0.00376992	-	0.00061697
	0.00572998	0.00137664	0.00246168				0.03565209	
1s2s(3S)4s	0.01940873	0.00409526	0.00869825	-	0.00553522	-	0.11487859	-
				0.04940928		0.01994925		0.00387020
1s2p(1P)3p	0.01967428	-	0.02171274	-	0.11801469	-	0.01133384	0.04698363
		0.05209977		0.06718630		0.10704774		
1s2p(3P)3p	-	0.09177676	-	0.12055957	0.06151645	0.19592577	-	0.02946129



	r		r	r	r	r	r	r
	0.03443899		0.03817778				0.01830340	
1s2p(1P)4p	0.01271526	0.00718747	0.03102852	-	-	0.03470682	-	-
				0.12645376	0.18641365		0.07269645	010891014
1s2p(3P)4p	-	-	-	0.22038406	-	-	0.12557346	-
	0.02292648	0.01305111	0.05502642		0.10883301	0.07285273		0.06946976
1s3p(1P)4p	0.13416475	0.17088706	0.07928252	0.31980580	0.71147913	-0.8430076	0.20336807	0.42316175
1s3p(3P)4p	-	-	-	-	0.40593028	0.18672502	-	0.25671607
	0.23300803	0.29819494	0.13992715	054042691			0.33719027	
1s3d(1D)4d	0.14523876	0.00531134	-	0.21550423	0.44411576	-	-	-
			0.17432880			0.07894099	0.36812603	0.73465699
1s3d(3D)4d	-	0.00890403	0.30160344	-	0.25802594	0.17184973	0.58936089	-
	0.25157219			036783272				0.44192886

Table-3: Excitation Energy, Optical Oscillator strengths (fl and fv) for the transition $1s^22s \rightarrow 1s 2s^2$ and $1s^22s \rightarrow 1s^22p$ in Be+

System	Present CI			Othe	er Theoretica	1
Be+	$\Delta E(eV)$	fL	fv	$\Delta E(eV)$	fL	fv
$1s^22s \rightarrow 1s$	474.405	0.0	0.0	*	*	*
2s ²				56.953	0.0	0.0
				* *		
				293.5		
$1s^22s^2 \rightarrow$	12.415	0.142		*	*	*
1s ² 2p				1.872	0.767	0.790
				**	**	**

* Theoretical Result for Be⁺ ionic atom.

** Theoretical Result for C³⁺ ionic atom.

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