SCF TREATMENT OF HIGHER EXCITED STATES OF ATOMS. TRANSITION PROBABILITIES BETWEEN EXCITED STATES OF Si II*

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(Received January 17, 1978)

A nonrelativistic SCF method for higher excited states of atoms has been developed with orthogonality constraints for states of the same symmetry. The two-by-two rotation method was adapted for this purpose, where the mixing of subshells replaces mixing of orbitals. This method was applied to several states of Si II. Oscillator strenghts of transitions between ns and $n'p$ states for n, n' varying from 4 to 7 were calculated.

1. Introduction

The problem of calculating the wave functions for higher excited states of a many electron atom is associated with some nontrivial technical difficulties. To solve the problem several methods have been developed. Very useful and simple are semiempirical methods, like the method of Weinstein [1] and its extensions [2]. On the other hand, we have the ab initio treatments which are better grounded physically. The most sophisticated ab initio treatments are based on the configuration interaction (CI) [3]. However, a large scale configuration interaction is (because of the slow covergence) tiresome and expensive, and a very limited one might again be insufficient. For this reason there is increasing interest in SCF-type calculations for excited states, with eventual improvement of the excited state by a configuration interaction. It has been shown that such an improvement is easy to perform [4]. In fact, the SCF treatment of excited states can even interchange the order of the states when compared with results of CI limited to a few configurations [5].

* The study was supported in part by the Polish Ministry of Science, Technique and Education under Contract No MR I/5 and in part through the M. Curie-Skłodowska found by the National Bureau of Standards, USA.

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The SCF treatment developed in this paper is based on Rossi's two-by-two rotation method [6]. Instead of mixing pairs of orbitals, however, we are going to mix occupied and virtual subshells of the same l. Subshells are mixed as long as a minimization of the total configuration state energy is achieved, up to a threshold. Because of mixing subshells rather than orbitals, the formalism of the Rossi method had to be slightly changed.

2. Method

The average configuration state energy is rotationally invariant. For this reason atomic orbitals have the familiar form here

$$\frac{1}{r} R_{nl}(r) Y_{lm}(\vartheta, \varphi),$$

with a hydrogenlike angular part. The purpose of the SCF treatment is to find the optimal radial part R_{nl} of each occupied subshell nl. In this work we asume the analytical approximation, expressing radial parts by linear combinations of Slater functions

$$R_{nl}(r) = \sum_{t=1}^{N} c_{nlt} \varphi_t(r), \tag{1}$$

where

$$\varphi_t(r) = r^{n_t^*} \exp(-a_t r). \tag{2}$$

Slater-type expansions are known already for many atoms and ions, at least for the case of the ground state. In the case of SiII, for example, the appropriate expansion has been by Clementi [7]. Radial parts of $1s$, $2s$ and $2p$ subshells are expanded there into three such terms whereas those of $3s$ and $3p$ into two terms. When dealing with excited states we must introduce new terms of type (2), optimizing the exponent a_t variationally or estimating it with the help of a physically sound model. It was found satisfactory in this work to estimate a_t from the familiar Rydberg formula, according to which

$$I_t = \frac{me^4 Z_{\text{eff}}^2}{2\hbar^2 n_t^2} = \frac{me^4 a_t}{2\hbar^2}. \tag{3}$$

The ionization energies were taken from the tables of Moore [8].

The set of radial parts obtained in this way is not orthogonal. For this reason the radial parts were orthogonalized with the help of the Schmidt procedure [9]. In this procedure one starts with ground state orbitals (one orthogonal to the other) and adds the excited state orbitals, one at a time, in the order of increasing energies. Discussing SiII up to 20 Slater-type functions were used, constructing in this way the starting radial parts of subshells $1s-11s$ and $2p-11p$.

For any given electronic configuration of an atomic system the energy in the independent particle approximation is [10]

$$E = \sum_{n,l} N_{nl} I_{nl} + \tfrac{1}{2} \sum_{\substack{n_1,l_1,\\ n_2,l_2,\\ k}} [\alpha_k(n_1 l_1, n_2 l_2) F^k(n_1, l_1, n_2, l_2) - \beta_k(n_1 l_1, n_2 l_1) G^k(n_1, l_1, n_2, l_2)], \quad (4)$$

where N_{nl} is the number of electrons in the subshell nl,

$$I_{nl} = \int_0^\infty R_{nl}(\gamma) \left[-\tfrac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] R_{nl}(r) dr, \quad (5)$$

$$F^k(n_1, l_1, n_2, l_2) = \int_0^\infty \frac{r_<^k}{r_>^{k+1}} R^2_{n_1 l_1}(r_1) R^2_{n_2 l_2}(r_2) dr_1 dr_2, \quad (6)$$

$$G^k(n_1, l_1, n_2, l_2) = \int_0^\infty \frac{r_<^k}{r_>^{k+1}} R_{n_1 l_1}(r_1) R_{n_2 l_2}(r_1) R_{n_1 l_1}(r_2) R_{n_2 l_2}(r_2) dr_1 dr_2, \quad (7)$$

and where all values are defined in atomic units. Coefficients α_k and β_k are connected with angular parts of orbitals and of the interaction operator. They can be expressed as follows [10]

$$\alpha_k(n_1 l_1, n_2 l_2) = \delta_{k0} N_{n_1 l_1} N_{n_2 l_2} \quad (8)$$

$$\beta_k(n_1 l_1, n_2 l_2) = \frac{N_{n_1 l_1} N_{n_2 l_2}}{2(2l_1+1)(2l_2+1)} (l_1 \| C^k \| l_2)^2. \quad (9)$$

The coefficients c_{nlt} (1) are the linear variational parameters. In the SCF procedure we always started from the functions found by Clementi for ground state orbitals and that for the appropriate orthogonalized exicted state. Then, following the idea of Rossi, radial parts of two different subshells of the same l were mixed, in order to gain a decrease in energy

$$\begin{pmatrix} R'_{n_i l_i} \\ R'_{n_j l_j} \end{pmatrix} = \begin{pmatrix} \cos\theta_{ij} & \sin\theta_{ij} \\ -\sin\theta_{ij} & \cos\theta_{ij} \end{pmatrix} \begin{pmatrix} R_{n_i l_i} \\ R_{n_j l_j} \end{pmatrix}, \quad (10)$$

where $l_i = l_j$. The mixing was carried out in steps, each mixing involving one of the partly or fully occupied subshells with a virtual one. By virtual subshells we mean here all subshells with the energy level above the excited orbital level first discussed; in this way the mutual orthogonality of all excited states and the ground state is guaranteed somehow automatically. Owing to this restriction on mixing the lowest possible estimate of the excited state energy is not necessarily obtained. It was found, however, that the most significant part of relaxation of the orbitals is included in this way, both of core orbitals

and the excited one, particularly when dealing with one electron outside a closed-shell core.

The mixing angle θ_{ij} follows from the condition of minimum of energy (4)

$$\frac{\partial E(\theta_{ij})}{\partial \theta_{ij}} = 0. \tag{11}$$

The appropriate expression is fairly complicated. However, its derivation is straightforward; it suffices to consider in equation (4) the derivatives of all I_{nl}'s, $F^k(n_1, l_1, n_2, l_2)$'s and $G^k(n_1, l_1, n_2, l_2)$'s with respect to θ_{ij}. For this reason the detailed expression for this derivative is not given in this article.

3. Iteration schemes

Solution of the set of equations (11) for all possible mixing agles simultaneously, is the bottleneck of the treatment, being the most time consuming part of the SCF scheme. For this reason three different iterative schemes had been considered in this work.

In scheme I all possible mixings had been considered in a preliminary discussion and finally that one which yielded the largest decrease in energy was selected. For this pair of subshells the mixing of the radial parts had been performed. The procedure was then repeated again and again until, for each type of subshells (s, p, etc.) separately, selfconsistency was achieved.

In scheme II the steepest descent method was applied, in the formulation given by Garton and Sutcliffe [11]. Suppose that θ_{ij} is the mixing angle of radial parts $R_{n_il_i}(r)$ and $R_{n_jl_j}(r)$, and that we are discussing the hyperspace spanned by all possible angles θ_{ij}. In this scheme the negative derivative

$$-\left(\frac{\partial E}{\partial \theta_{ij}}\right)_{\theta_{ij}=0} \tag{12}$$

is the component of a gradient showing the expected direction towards the minimum of energy (a component of a generalized force).

In scheme III not the force itself was the criterium of the degree of mixing, but rather the possible lowerings of energy in the independent treatment. Now, if

$$G_{ij} = \sin \theta_{ij}^0, \tag{13}$$

where θ_{ij}^0 is the mixing angle optimal for the independent mixing of $R_{n_il_i}$ and $R_{n_jl_j}$ then

$$R'_{n_il_i} = (1+\lambda^2 \sum_{\substack{j \\ (j>i)}} G_{ij}^2)^{-\frac{1}{2}}(R_{n_il_i}+\lambda \sum_{\substack{j \\ (j>i)}} G_{ij}R_{n_jl_j}), \tag{14}$$

where λ is a variational parameter. As in the former schemes $l_j = l_i$ for all j's.

It may happen (in the case of schemes II and III) that new orbitals cease to be orthogonal to one another. In such a case they are orthogonalized symmetrically by the Löwdin orthogonalization procedure [9] which keeps the orbitals unchanged as much as possible. Virtual orbitals are then reorthogonalized (in scheme II and III) by the somewhat simpler Schmidt procedure. The final value of $E_{\min}$ is then calculated, based on the reorthogonalized orbitals. The procedure is repeated again and again until the gain in energy in a single step is negligible.

The method described was applied to excited states $4s-7s$ and $4p-7p$ of SiII. In test calculations it was found that scheme III is definitely the fastest one and the steepest descent scheme II the slowest one. For this reason scheme III was exclusively used in all subsequent calculations.

4. Results and discussion

In Table I the calculated and observed excited state energies are compared with each other, relative to the ground state. As follows from the table, agreement of the presented SCF-type calculations with experiment is satisfactory on the order of 0.01 a.u. The remaining

TABLE I

Values of energy of excitation for SiII in a. u.

Energy level	Our results	Moore
$3p$	0.0	0.0
$4p$	0.361	0.369
$5p$	0.459	0.472
$6p$	0.504	0.519
$7p$	0.528	—
$4s$	0.290	0.297
$5s$	0.432	0.455
$6s$	0.490	0.506
$7s$	0.520	0.536

discrepancy is evidently due to unballanced changes of the correlation energy in the ground state and the appropriate excited state.

Table II contains a set of oscillator strengths (in the dipole moment and dipole velocity approximation) and appropriate life times. The calculated values are compared where possible, with scanty experimental data and with results of other calculations.

It is hard to draw decisive conclusions from this comparison. The agreement with experiment is certainly not worse then the scatter in experimental data and the results obtained in the dipole moment approximation are similar to those from the dipole velocity approximations. Where CI values have been reported (for $3p \rightarrow 4s$, $3p \rightarrow 5s$, $4p \rightarrow 4s$), they are usually close to those calculated in this work. It is somewhat interesting that in general

TABLE II

Oscillator strenghts for Si II

Transitions	$g_{nl} f_{nln'l'}$		
	Our results $\left(\frac{\text{dipole moment}}{\text{dipole velocity}}\right)$	Other results (see Ref.)	Method
$3p - 4s$	0.651 0.666	0.651 [3] 0.678 [2] 0.779 [12]	CI semiempirical exp.
$3p - 5s$	0.101 0.101	0.127 [3] 0.0966 [2]	CI sem.
$3p - 6s$	0.0405 0.0408	0.0345 [2]	sem.
$3p - 7s$	0.0154 0.0151	0.0168 [2]	sem.
$4p - 5s$	1.431 1.348	1.561 [14] 1.442 [2] 1.51 [15] 1.32 [16]	HF sem. exp. exp.
$4p - 6s$	0.186 0.171	0.172 [2] 0.150 [17]	sem. CA (Coulomb appr.)
$4p - 7s$	0.0486 0.0450	0.0599 [2]	sem.
$5p - 6s$	2.182 2.246		
$5p - 7s$	0.153 0.182	0.228 [17]	CA
$3p - 7s$	2.665 2.903		
$4s - 4p$	2.767 2.344	2.71 [3] 2.662 [2] 2.370 [15] 3.0 [20]	CI sem. exp. exp.
$4s - 5p$	0.0049 0.0015	0.000228 [2]	sem.

TABLE II (continued)

Transitions	$g_{nl}f_{nln'l'}$		
	Our results $\left(\frac{\text{dipole moment}}{\text{dipole velocity}}\right)$	Other results (see Ref.)	Method
$4s - 6p$	$\frac{0.00000842}{0.000352}$	0.00112 [2]	sem.
$4s - 7p$	$\frac{0.0000896}{0.0006238}$		
$5s - 6p$	$\frac{3.5005}{3.3679}$		
$5s - 6p$	$\frac{0.0103}{0.0085}$		
$5s - 7p$	$\frac{0.000209}{0.000016}$		
$6s - 6p$	$\frac{3.970}{4.790}$		
$6s - 7p$	$\frac{0.06615}{0.01594}$		
$7s - 7p$	$\frac{5.492}{4.481}$		

also a good agreement exists between the presented ab initio calculation and the simpler semiempirical one reported by Migdałek [2]. A more serious discrepancy appears only in the case of vanishingly small oscillator strengths like for transitions $4s \to 5p$, $4s \to 6p$ and $4s \to 7p$. It is difficult to say, at the moment, which of the results agree better with experiment because of the lack of appropriate data. With regard to the life time, it is practically within the experimental error in the case of the $4s$ excited state. In the case of the $3p \to 5s$ excitation, on the other hand, the experimental value is roughly half of the calculated one.

In many other cases neither theoretical nor experimental values exist with which one can compare. In all these cases the present work gives a first estimation of appropriate oscillator stengths and the life-times.

The author is greatly indebted to Professor A. Gołębiewski for helpful discussions.

TABLE III

Life times for SiII

Level	$\tau_{nl} \times 10^{-9}$ sec		
	Our results $\left(\frac{\text{dipole moment}}{\text{dipole velocity}}\right)$	Other results (see Ref.)	Method
$4s$	$\frac{1.13}{1.11}$	1.5 ±0.3 [13] 0.9 ±0.2 [12] 1.0 [2]	exp. exp. sem.
$5s$	$\frac{2.337}{2.417}$	0.97±0.2 [13]	exp.
$6s$	$\frac{4.136}{4.172}$		
$7s$	$\frac{9.307}{9.300}$		
$4p$	$\frac{4.588}{5.419}$		
$5p$	$\frac{23.68}{25.52}$		
$6p$	$\frac{83.29}{69.40}$		
$7p$	$\frac{132.2}{170.4}$		

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