

氫至氙各原子振盪強度總數 $S(2)$ 值
Oscillator Strength Sum $S(2)$: H-Xe

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ABSTRACT — Numerical evaluations of oscillator strength sum $S(2)$ for atoms with atomic number $Z \leq 54$ are facilitated. Clementi's analytical functions expanded in the Roothaan-Hartree-Fock method are used to give an approximate representation of atomic orbitals.

The oscillator strength sum $S(K)$ may be defined in terms of the matrix element of the electron dipole-moment operator R between two states J and J' [1-3],

$$S(K) = \frac{2}{3} \sum_{J'} \langle JM | R^{(1)} | J'M' \rangle \langle J'M' | R^{(1)} | JM \rangle (E_{J'} - E_J)^{K+1} \quad (1)$$

where the summation is over all excited discrete and continuous states with selection rules $J'=J, J \pm 1$ and $M=2J+1$. Numerical results of sums $S(-3)$ through $S(-1)$ for atoms He-Kr have been evaluated by Cummings [4]. $S(0)$ equals the number of electrons in the atom, known as the famous Thomas-Reiche-Kuhn oscillator strength sum rule. For $K > 2.5$, $S(K)$ becomes infinite [3].

A number of relations have been obtained relating the average dispersion coefficient [5]. Of these, one of the best approximations is expressed in terms of $S(-1.5)$. The graphs of the spectral density of oscillator strength against the energy have been constructed by Bethe [6] and by Fano [3]. The curve in such a graph increases monotonically with a finite nonzero slope in the continuous spectrum. From the graphs and the moment ratios $\frac{S_{r+1}}{S_r} = \frac{S_r}{S_{r-1}} > 1$, presented by Fano [3], it was thought the values of $S(-1.5)$ could be obtained from an appropriate quantitative relation between $S(K)$ and K . In the present paper numerical evaluations of $S(2)$ for atoms H-Xe are facilitated. Atomic units are used throughout this article.

The derivation proceeds by exploiting the operator algebra and some identities of commutators, e.g., $[H, X] = -\frac{i\hbar}{m} P_x$, $[H, P_x] = i\hbar \frac{\partial}{\partial x} V(x, y, z)$. Then we have

$$\begin{aligned} \langle J | X | J' \rangle \langle J' | X | J \rangle (E_{J'} - E_J)^2 &= -\langle J | [H, X] | J' \rangle \langle J' | [H, X] | J \rangle \\ &= \langle J | P_x | J' \rangle \langle J' | P_x | J \rangle. \end{aligned} \quad (2)$$

$$\langle J | [H, P_x] | J' \rangle = \langle J | P_x | J' \rangle (E_J - E_{J'}) \quad \text{or}$$

$$\langle J' | [H, P_x] | J \rangle = \langle J' | P_x | J \rangle (E_{J'} - E_J). \quad (3)$$

Therefore a preliminary expression of S(2) can be expressed by

$$\begin{aligned} \langle J | X | J' \rangle \langle J' | X | J \rangle (E_J - E_{J'})^3 &= \langle J | P_x | J' \rangle \langle J' | P_x | J \rangle (E_{J'} - E_J) \\ &= \frac{1}{2} \langle J | \frac{\partial^2}{\partial x^2} V | J \rangle. \end{aligned} \quad (4)$$

For a N-electron atom the electron potential V of the electrons is represented by

$$V = - \sum_i \frac{Ze^2}{r_i} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{r_{ij}}, \quad (5)$$

where the factor $\frac{1}{2}$ avoids counting the same interelectron repulsions twice. Inter-electron potentials yield no net contribution to $\langle J | \frac{\partial^2}{\partial x^2} V | J \rangle$ since the partial derivative with respect to x of the second terms in (5) for a certain electron k ($k=j \neq i$) is zero, i.e.,

$$\frac{\partial}{\partial x_k} \left(\frac{1}{2} \sum_i \sum_{j \neq k} \frac{e^2}{r_{ij}} \right) = - \frac{1}{2} \sum_i \left(\frac{e^2}{r_{ki}^2} \frac{\partial r_{ki}}{\partial x_k} + \frac{e^2}{r_{ik}^2} \frac{\partial r_{ik}}{\partial x_k} \right) = 0 \quad (6)$$

The Poisson's equation connects the electrostatic potential V with charge density ρ . With suitable rearrangement this is

$$\frac{\partial^2}{\partial x^2} V = \frac{\partial^2}{\partial x^2} \left(- \sum_i \frac{Ze^2}{r_i} \right) = 4\pi Z \left[\sum_i \rho(x_i) \right]. \quad (7)$$

The boundary conditions for which (7) must be solved are given by the field at the nucleus and only the s wavefunctions are nonzero there [7]. The three dimensional Dirac delta function $\delta(r)$ picks out this region and whose mean value is the electron density at the nucleus. Thus the expression of S(2) for atom in its ground state, much easier to be achieved than that in its excited states, yields

$$\begin{aligned} S(2) &= \frac{2}{3} \sum_{J'} \langle J | \sum_i \frac{1}{r_i} | J' \rangle \langle J' | \sum_i \frac{1}{r_i} | J \rangle (E_J - E_{J'})^3 \\ &= \frac{4}{3} \pi Z \langle J | \sum_i \delta(r_i) | J \rangle \\ &= \frac{4}{3} \pi Z \rho_{\text{total}}(0), \end{aligned}$$

where $\rho_{\text{total}}(0)$ is the total electron density at the nucleus in an atom.

Since the spherical harmonics $Y_l^m(\theta, \phi)$ are normalized to unity, the electron density at the nucleus for a given orbital $\rho_{\text{orb}}^u(0)$ can be expressed in

terms of a given radial distribution function $R_{n\ell}(r)$,

$$\rho_{orb}^u(0) = \lim_{R \rightarrow 0} \frac{\int_0^R (R_{n\ell}(r))^2 r^2 dr}{\frac{4}{3} \pi R^3} \cdot P(u) \quad (9)$$

where $P(u)$ is the electron occupation number of orbital u . For H-like atoms, $\rho_{orb}^u(0)$ can be expressed by

$$\rho_{orb}^u(0) = \lim_{R \rightarrow 0} \frac{3}{4\pi} \left(\frac{b_0^2}{2\ell+3} R^{2\ell} + \frac{2b_0 b_1}{2\ell+4} R^{2\ell+1} + \dots + \frac{b_q^2}{2\ell+3+2q} R^{2\ell+2q} \right), \quad (10)$$

where $q = n - \ell - 1$ [8]. This expression is zero unless the azimuthal quantum number of orbital ℓ equals 0. Hence we are only interested in $\ell = 0$ or s states. The explicit expression of $\rho_{total}(0)$ for H-like atoms yields finally,

$$\rho_{total}(0) = \rho_{orb}^u(0) = \frac{b_0^2}{4\pi} = \frac{Z^3}{n^3 \pi} \quad (11)$$

The constant b_0 is determined by normalization.

The orbital wavefunction ϕ in Clementi's analytical functions is expanded in terms of Slater type orbital (STO) in which the radial functions is written

$$R_{n\ell}(r) = CNr^{n-1} \exp(-\xi \cdot r). \quad (12)$$

Values of both STO expansion coefficient C and orbital exponent ξ for atoms with $Z \leq 54$ are tabulated in 1974 [9]. In terms of STO, $\rho_{orb}^u(0)$ is written

$$\rho_{orb}^u(0) = \sum_{ij} \sum_{i'j'} C_i C_{i'} N_i N_{i'} \lim_{R \rightarrow 0} \frac{\int_0^R r^{n_i-1} r^{n_{j'}-1} r^2 dr}{\frac{4}{3} \pi R^3} \cdot P(u), \quad (13a)$$

this expression is zero unless the principal quantum number of STO equals 1, i.e., $n_i = n_{j'} = 1$. Thus we have a simpler form:

$$\rho_{orb}^u(0) = \frac{1}{\pi} \sum_{ij} C_i C_j (\xi_i)^{3/2} (\xi_j)^{3/2} \cdot P(u) \quad (13b)$$

The explicit expression of $\rho_{total}(0)$ for polyelectron atoms yields finally

$$\rho_{total}(0) = \sum_u \rho_{orb}^u(0) = \frac{1}{\pi} \sum_{uij} C_i C_j (\xi_i)^{3/2} (\xi_j)^{3/2} \cdot P(u). \quad (14)$$

Notice we are only interested in s states as mentioned above.

Fischer has tabulated values of a property $A_{n\ell}$, known as Fischer's numerical Hartree-Fock (H-F) functions [10]. For a given orbital $n\ell$, $A_{n\ell}$ is defined

by

$$A_{n\ell} = \lim_{r \rightarrow 0} P_{n\ell}(r) / r^{\ell+1} \quad (15)$$

Legendre polynomial $P_{n\ell}(r)$ equals $r \cdot R_{n\ell}(r)$. In terms of $A_{n\ell}$, we then obtain

$$\rho_{\text{orb}}^u(0) = \frac{A_{n\ell}^2}{4\pi} P(u) \quad \text{and} \quad (16)$$

$$\rho_{\text{total}}(0) = \sum_u \rho_{\text{orb}}^u(0) = \sum_u \frac{A_{n\ell}^2}{4\pi} P(u). \quad (17)$$

With the aid of analytical functions expanded in the Roothaan-Hartree-Fock method [9] numerical results of S(2), represented by exponential notation, are evaluated,

Atom	Sum S(2)	Atom	Sum S(2)	Atom	Sum S(2)	Atom	Sum S(2)	Atom	Sum S(2)
He 1S	0.301366E2	Al 2P	0.763942E5	Cr 5D	0.936794E6	Br 2P	0.433551E7	Rh 4F	0.120119E8
Li 2S	0.173846E3	Si 3P	0.104546E6	Mn 6S	0.110579E7	Kr 1S	0.485990E7	Pd 3F	0.131305E8
Be 1S	0.593597E3	P 4S	0.137370E6	Fe 5D	0.129727E7	Rb 2S	0.542818E7	Ag 2D	0.143258E8
B 2P	0.150764E4	S 3P	0.178950E6	Co 4F	0.151193E7	Sr 1S	0.605000E7	Cd 1S	0.156042E8
C 3P	0.320582E4	Cl 2P	0.229154E6	Ni 3F	0.175256E7	Y 2D	0.672288E7	In 2P	0.169667E8
N 4S	0.604419E4	Ar 1S	0.289546E6	Cu 2S	0.201973E7	Zr 3F	0.745049E7	Sn 3P	0.194520E8
O 3P	0.104544E5	K 2S	0.361202E6	Zn 1S	0.231832E7	Nb 4F	0.823309E7	Sb 4S	0.199467E8
F 2P	0.169160E5	Ca 1S	0.445680E6	Ga 2P	0.264745E7	Mo 5D	0.908125E7	Te 3P	0.215800E8
Ne 1S	0.259766E5	Sc 4F	0.543826E6	Ge 3P	0.301197E7	Tc 6S	0.999037E7	I 2P	0.233117E8
Na 2S	0.384203E5	Ti 3F	0.657412E6	As 4S	0.341291E7	Ru 5D	0.109664E7	Xe 1S	0.251447E8
Mg 1S	0.549769E5	V 4F	0.787918E6	Se 3P	0.385397E7				

In a given atom the computed results of $\rho_{ns}(0)$ decrease sharply with increasing principal quantum number of s orbitals, e.g., $\rho_{1s}(0)$, $\rho_{2s}(0)$, $\rho_{3s}(0)$, $\rho_{4s}(0)$, and $\rho_{5s}(0)$ for Xe are 1.79865, 293.866, 1764.08, 14432.4, and 49108.5 a.u., respectively. In a given s orbital, those of $\rho_{ns}(0)$ increase gradually with increasing atomic number except those of $\rho_{4s}(0)$ for Co and Cu are a little smaller than those of corresponding elements due to low electron occupation number which equals 1 in these two atoms. Values of S(2), consequently, increase with increasing atomic number as shown in table. We also obtain a good agreement between the two H-F results, the maximum difference is 0.14%. In a given range the deviations between H-like results and H-F results decrease at first rapidly and then slowly as the atomic number is increased. The minimum deviation for 1s orbitals is 2.1% of Xe, that for 2s orbitals is 20.7% of Xe. In other words, H-F 1s orbitals are H-like near the nucleus especially for the heavier atoms.

Upon achieving numerical results of both S(2) and S(1) we expect to obtain a quantitative relation between S(K) and K from the known values of sums S(-2) through S(2). Further numerical evaluations of S(1) are studied in our later work.

References

1. B. W. Shore & D. H. Menzel, "Principles of Atomic Spectra", Wiley, New York, 1967, 473-476.
2. R. Jackiw, Phys. Rev., 157, 1220 (1967).
3. U. Fano & J. W. Cooper, Rev. Mod. Phys., 40, 441 (1968).
4. F. E. Cummings (private communication).
5. See, for example, A. Dalgarno, Advan. Chem. Phys., 12, 143 (1967); R. G. Gordon, J. Chem. Phys., 54, 663; 54, 4517 (1971); J. H. Miller & H. P. Kelley, Phys. Rev., A5, 516 (1972).
6. Hans A. Bethe, "Intermediate Quantum Mechanics", Benjamin, New York., 1964.
7. J. Thouless, "The Quantum Mechanics of Many-body System", Academic Press, New York., 1961.
8. I. N. Levine, "Quantum Chemistry," Vol. I, Allyn & Bacon, Boston, 1970.
9. E. Clement, "Atomic Data and Nuclear Data Tables", 14, Nos. 3-4, 177 (1974).
10. C. Froese-Fischer, "Some Hartree-Fock Results for the Atoms He-Rn", Dept. of Applied Mathematics, Univ. of Waterloo, Waterloo, Ontario, 1968.

多時間微擾理論及其在非諧和振子之應用

Studies on the Multiple-Scale Perturbation Theory and Its Application to the Anharmonic Oscillator

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ABSTRACT — In this article of the works on the anharmonic oscillator, a multiple-time-scale perturbation method, which is originally introduced by Krylov and Bogoliubov to solve the problems in nonlinear mechanics, is applied. It is seen that the results obtained agree completely with those of Landau and Lifshitz.

The multiple-time-scale perturbation theory (MTSPT) was first introduced by Krylov and Bogoliubov [1] to solve problems in nonlinear mechanics. Friedman [2] and Sandri [3] extended this method and applied it to the kinetic theory of gases and plasmas. Recently, Y. C. Lee [4][5] et al. applied the MTSPT to the spontaneous radiation process. The results obtained by the MTSPT agree completely with the previous results. The main purpose of this paper is to study this powerful method and try to apply it to the familiar mechanic problems.