Theoret. chim. Acta (Berl.) 5, 455—458 (1966)

Application of Z^{-1} Expansion Method to $1s3d\ {}^1D$ and ${}^3D$ States of Helium: Configuration Interaction Calculation and Correlation Energy

N. K. Das Gupta

Department of Chemistry, Visva-Bharati University, Shanti-Niketan, West Bengal, India

M. A. Ali

Department of Chemistry, Sheffield University, Sheffield, England

Received May 2, 1966

Recently, there has been considerable interest in the application of the Z^{-1} expansion method to excited states of the Helium isoelectronic sequence, following the pioneering works of Hylleraas [1]. Sharma and Coulson [2] used this method for obtaining Z^{-1} expansion of correlation energy in $1s2s\ {}^1S$ and ${}^3S$ states of helium. Knight and Scherr [3] extended the calculation of Sharma and Coulson to other excited states of He like systems using more elaborate variation-perturbation functions in well known Hylleraas coordinates. Perrin and Stewart [4] used the alternative method of superposition of configurations to $1s2s$ ${}^1S$ and ${}^3S$ states, $1s2p\ {}^1P$ and ${}^3P$ states of helium and conclude that for excited states the method of superposition of configurations compares favourably with the results obtained from using the method of incomplete separation of variables. In the present paper, we report the results of calculations on $1s3d\ {}^1D$ and ${}^3D$ states of helium by the method of superposition of configurations.

Theoretical Basis: The fundaments of the method are well known [5, 6] and are given very briefly. Using scaled coordinates $R_i = Z \cdot r_i$, $R_{12} = Z \cdot r_{12}$, the non-relativistic Schrödinger equation of a two-electron atom is

$$H' \Psi' = E' \Psi'$$

where

$$H' = H'_0 + H'_1 \ ; \quad E = Z^2 E'$$

with

$$H'_0 = \sum_{i=1}^{2} \left(-\tfrac{1}{2} \nabla_i'^2 - \frac{1}{R_i} \right), \qquad H'_1 = \frac{1}{Z} \cdot \frac{1}{R_{12}}$$

the prime denoting the use of scaled coordinates. Treating H'_1 as a perturbation on H'_0 with Z^{-1} having the role of perturbation parameter, we can expand Ψ' and E' in powers of Z^{-1}:

$$\Psi' = \Psi_0 + \frac{1}{Z} \Psi_1 + \frac{1}{Z^2} \Psi_2 + \dots$$

$$E' Z^2 = E = E_0 Z^2 + E_1 Z + E_2 + E_3 \cdot Z^{-1} + \dots$$

The zero order functions are

$$\Psi_0({}^1D) = \frac{1}{\sqrt{2}}\,[1s_H(1)\,3d_H(2) + 3d_H(1)\,1s_H(2)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]\,,$$

$$\Psi_0({}^3D) = \frac{1}{\sqrt{2}}\,[1s_H(1)\,3d_H(2) - 3d_H(1)\,1s_H(2)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)]\,.$$

The subscript H indicates that we are using hydrogenic orbitals. The zero order energy E_0 for both cases is

$$E_0 = -\frac{1}{2} - \frac{1}{18} = 0.555555\,.$$

The first order energy contribution $E_1 = \langle\Psi_0 \mid H_1' \mid \Psi_0\rangle$ is easily obtained using the table of integrals given in Crossley and Coulson [5]:

$$E_1\,({}^1D) = 0.111270$$

$$E_1\,({}^3D) = 0.110776\,.$$

For obtaining E_2 and E_3, we need to know Ψ_1 or some approximation to it. For approximating Ψ_1 we can use the Hylleraas variational principle, i.e. for any trial Ψ_1^{tr}:

$$\varepsilon_2(\Psi_1^{tr}) = \langle\Psi_1^{tr} \mid H_0' - E_0 \mid \Psi_1^{tr}\rangle + \langle\Psi_1^{tr} \mid H_1' - E_1 \mid \Psi_0\rangle + \langle\Psi_0 \mid H_1' - E_1 \mid \Psi_1^{tr}\rangle \geqslant E_2\,.$$

If we write Ψ_1^{tr} as a linear superposition of configurational functions Φ_k which are normalised but not necessarily orthogonal to Ψ_0, the application of the Hylleraas principle leads to a solution of a linear equation system for the linear coefficients of combination:

$$\sum_l C_l\,\langle\Phi_k \mid H_0' - E_0 \mid \Phi_l\rangle = E_1\,\langle\Phi_k \mid \Psi_0\rangle - \langle\Phi_k \mid H_1' \mid \Psi_0\rangle\,.$$

Once an approximate $\tilde{\Psi}_1$ has been obtained, E_2 and E_3 are approximately given by

$$\tilde{E}_2 = \langle\tilde{\Psi}_1 \mid H_1' \mid \Psi_0\rangle - \langle\tilde{\Psi}_1 \mid \Psi_0\rangle\,E_1\,,$$

$$\tilde{E}_3 = \langle\tilde{\Psi}_1 \mid H_1' - E_1 \mid \tilde{\Psi}_1\rangle - 2\,\langle\Psi_0 \mid \tilde{\Psi}_1\rangle\,\tilde{E}_2\,.$$

Variational Evaluation of $\tilde{\Psi}_1$. For the expansion of the non-relativistic exact energy, we take Ψ_1^{tr} as

$$\Psi_1^{tr} = \sum_{i=1}^{8} C_i\,\Phi_i$$

where

$$\Phi_1 = \frac{1}{\sqrt{2}}\,[1s_H(1)\,4d(2) \pm 4d(1)\,1s_H(2)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) \mp \beta(1)\,\alpha(2)]\,,$$

$$\Phi_2 = \frac{1}{\sqrt{2}}\,[1s_H(1)\,5d(2) \pm 5d(1)\,1s_H(2)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) \mp \beta(1)\,\alpha(2)]\,,$$

$$\Phi_3 = \frac{1}{\sqrt{2}}\,[2s(1)\,3d_H(2) \pm 3d_H(1)\,2s(2)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) \mp \beta(1)\,\alpha(2)]\,,$$

$$\Phi_4 = \frac{1}{\sqrt{2}}\,[3s(1)\,3d_H(2) \pm 3d_H(1)\,3s(2)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) \mp \beta(1)\,\alpha(2)]\,,$$

$$\Phi_5 = \frac{1}{\sqrt{2}}\,[4s(1)\,3d_H(2) \pm 3d_H(1)\,4s(2)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\,\beta(2) \mp \beta(1)\,\alpha(2)]\,,$$

$$\Phi_6 = \frac{1}{\sqrt{2}}[2s(1)\quad 4d(2) \pm 4d(1)\quad 2s(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) \mp \beta(1)\alpha(2)]\,,$$

$$\Phi_7 = \frac{1}{\sqrt{2}}[2s(1)\quad 5d(2) \pm 5d(1)\quad 2s(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) \mp \beta(1)\alpha(2)]\,,$$

$$\Phi_8 = \frac{1}{\sqrt{2}}[3s(1)\quad 4d(2) \pm 4d(1)\quad 3s(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) \mp \beta(1)\alpha(2)]\,.$$

The symbols without subscript H denote Slater type orbitals with the same exponent as the corresponding hydrogenic orbital. The upper and lower signs are to be taken together for ^1D and ^3D states. In the Table we display the linear coefficients obtained by the application of the Hylleraas principle. The calculations were performed with a manual desk calculator with seven figure accuracy.

Using this variational approximation to $\tilde{\Psi}_1$, $\tilde{E}_2$ and $\tilde{E}_3$ are calculated leading to the following Z-expansions of energy:

Table. *Linear coefficients of* $\tilde{\Psi}_1$

C_i	^1D	^3D
C_1	3.7859611	3.6335554
C_2	−0.0157671	0.0409217
C_3	−0.0044327	0.0138210
C_4	−0.0049250	0.0157421
C_5	−0.0023154	0.0057918
C_6	0.0118267	−0.0389414
C_7	−0.0094759	0.0310555
C_8	0.0071514	−0.0214261

$$E(^1D) = -0.555555\cdot Z^2 + 0.111270\cdot Z - 0.056264 + 0.001046\cdot Z^{-1}\,,$$

$$E(^3D) = -0.555555\cdot Z^2 + 0.110776\cdot Z - 0.053945 - 0.002799\cdot Z^{-1}\,.$$

Discussion. PERRIN and STEWART [4] found that the contribution to E_2 and E_3 for $1s2p$ ^1P and ^3P states from angular configurations is very small. This is likely to be more so for the states under consideration here. The variation perturbation functions we employ would only recover radial correlation energy. The energy calculated using our E_2 and E_3 compares well with the very elaborate multiconfiguration variational calculation of GREEN, KOLCHIN and JOHNSON [7] (energy in a.u.):

State	Present calculation	GREEN, KOLCHIN and JOHNSON
^1D	−2.055423	−2.055615
^3D	−2.056014	−2.055630

This suggests that angular correlation energy is indeed small. It is to be noted that our calculated energy values do not provide an upper bound. However, an upper bound can be obtained [8] but the procedure usually leads to a poor upper bound. We are at present engaged in investigating the use of angular configurations for recovery of the greater part of angular correlation energy and hope to report the results in the near future.

Acknowledgement. We thank Professor S. C. SHOME, Presidency College, Calcutta for helpful discussions and constant encouragement. One of us (N.K.D.) gratefully acknowledges the award of Junior Research Fellowship from the Council of Scientific and Industrial Research, New Delhi, India during the tenure of which the present work was started.

References

[1] HYLLERAAS, E. A.: Z. Physik **65**, 209 (1930).
[2] SHARMA, C. S., and C. A. COULSON: Proc. physic. Soc. (London) **A80**, 81 (1962).
[3] KNIGHT, R. E., and C. W. SCHERR: Rev. mod. Physics. **35**, 431 (1963).
[4] PERRIN, R., and A. L. STEWART: Proc. physic. Soc. (London) **81**, 28 (1963).
[5] CROSSLEY, R. J. S., and C. A. COULSON: Proc. physic. Soc. (London) **81**, 211 (1963).
[6] LÖWDIN, P. O.: J. molecular Spectroscopy **3**, 46 (1959).
[7] GREEN, L. C., E. A. KOLCHIN, and N. C. JOHNSON: Physic. Rev. **139A**, 373 (1965).
[8] DALGARNO, A.: In Quantum theory, vol. 1, page 193, eqn. (149), (editor D. R. BATES). New York and London: Academic Press 1961.

Dr. M. A. ALI
Chemistry Department
The University
Sheffield 10, England