in electron-impact studies cannot hope to resolve clearly the rotational structure or determine the widths of auto-ionization lines. Although there does not appear to be a simple theoretical relationship between photoionization and electron-impact ionization of H (1*s*), it does experimentally appear to exist for all the simple diatomic molecules considered thus far, H_2, D_2, O_2, N_2, NO, and CO.

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Correlation Energies of the Lithium Sequence

C. D. H. Chisholm
Department of Chemistry, Glasgow University, Glasgow, Scotland

AND

A. Dalgarno*
School of Physics and Applied Mathematics, The Queen's University of Belfast, Belfast, Ireland

AND

F. R. Innes
Air Force Cambridge Research Laboratories, Bedford, Massachusetts

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The nonrelativistic eigenvalues of the $1s^22p\ ^2P$ states of the lithium sequence are calculated to be $E(Z)=-1.125Z^2+1.09352614Z-0.52717136+O(Z^{-1})$ a.u., where Z is the nuclear charge; and the energy of the $1s^22p\ ^2P$–$1s^22s\ ^2S$ transition is calculated to be $\Delta E(Z)=0.07072093Z-0.11902237+O(Z^{-1})$ a.u. For large nuclear charges, the addition of a $2p$ electron to the $1s^2\ ^1S$ core increases the magnitude of the correlation energy by 0.30 eV to give a value of 1.57 eV, most of which arises from the electron-pair energies.

1. INTRODUCTION

We have recently calculated the nonrelativistic eigenvalue of the $1s^22s\ ^2S$ states of the lithium sequence as a series in inverse powers of the nuclear charge Z, using a method that expresses the correlation energy as a weighted sum of electron-pair energies and certain single-electron nonadditive terms.[1] The addition of the $2s$ electron to the $1s^2\ ^1S$ core increases the magnitude of the correlation energy by 0.19 to 1.46 eV, most of which arises from the pair energies.

The method can be extended to states of higher angular momentum and in particular to the $1s^22p\ ^2P$ states of the lithium sequence.

2. THEORY

We choose a set of units in which the scale of distance is Z atomic units (a.u.) and the scale of energy is Z^2 a. u. If $\mathbf{r}_i$ is the position vector of the ith electron, the Hamiltonian is given by

$$H=H_0+V/Z\,, \tag{1}$$

where

$$H_0=-\tfrac{1}{2}\sum_{i=1}^{3}\nabla_i^2-\sum_{i=1}^{3}\frac{1}{r_i} \tag{2}$$

and

$$V=\sum_{i<j}^{3}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\,. \tag{3}$$

Then to second order in Z^{-1}, the energy E is given by

$$E(Z)=Z^2E_0+ZE_1+E_2\,, \tag{4}$$

where

$$E_1=\langle\psi_0|V|\psi_0\rangle\,, \tag{5}$$

$$E_2=\langle\psi_0|V-E_1|\psi_1\rangle\,, \tag{6}$$

ψ_0 and ψ_1 being the well-behaved solutions of

$$(H_0-E_0)\psi_0=0\,, \tag{7}$$

$$(H_0-E_0)\psi_1+(V-E_1)\psi_0=0\,. \tag{8}$$

The solution of (8) is

$$\begin{aligned}\psi_1(1s^22p\ ^2P)=\mathcal{A}\big[&\tfrac{1}{3}\sqrt{3}\{\psi_0(2p\ ^2P),\psi_1(1s^2\ ^1S)\}\\&-(\tfrac{1}{6}\sqrt{6})\{\psi_0(1s\ ^2S),\psi_1(1s2p\ ^1P)\}\\&+\tfrac{1}{2}\sqrt{2}\{\psi_0(1s\ ^2S),\psi_1(1s2p\ ^3P)\}\big]\,,\end{aligned} \tag{9}$$

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[*] Present address: Smithsonian Astrophysical Observatory and Harvard College Observatory, Cambridge, Mass.

[1] C. D. H. Chisholm and A. Dalgarno, Proc. Roy. Soc. (London) **A292**, 264 (1966).

where $\mathcal{A}$ is the antisymmetrizer and

$$\{\psi_0(nlSL),\psi_1(n'l'n''l''S'L')\}$$

is a vector-coupled product of the single-electron zero-order eigenfunctions ψ_0 and the antisymmetrized two-electron first-order eigenfunctions ψ_1.

If we define

$$y_k(\beta,\gamma|r)=r^{-k-1}\int_0^r \beta(s)\gamma(s)s^{k+2}ds+r^k\int_0^\infty \beta(s)\gamma(s)s^{1-k}ds \quad (10)$$

and

$$(\alpha\beta|A\gamma)_k=\int_0^\infty \alpha(r)y_k(\beta,\gamma|r)A(r)r^2dr \quad (11)$$

and use the procedures of Chisholm and Dalgarno,[1] it follows from substituting (9) into (6) that

$$E_2(1s^22p\ {}^2P)=E_2(1s^2\ {}^1S)+\tfrac{1}{2}E_2(1s2p\ {}^1P)+\tfrac{3}{2}E_2(1s2p\ {}^3P)+\zeta, \quad (12)$$

where

$$\zeta=4(1s2p|g2p)_0-\tfrac{2}{3}(2p1s|g2p)_1+\tfrac{1}{3}(1s1s|h2p)_1-\tfrac{1}{3}(1s1s|\theta 2p)_1+\tfrac{1}{2}(2p1s|\theta 1s)_0-\tfrac{3}{2}(2p1s|\phi 1s)_0; \quad (13)$$

in the labeling of the above matrix elements, $nl(r)$ represents the normalized hydrogen radial eigenfunctions, and

$$\left\{-\frac{1}{2}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)-\frac{1}{r}+\frac{1}{2}\right\}g(r)+y_0(1s,1s|r)1s(r)-\tfrac{5}{8}1s(r)=0, \quad (14)$$

$$\left\{-\frac{1}{2}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{2}{r^2}\right)-\frac{1}{r}+\frac{7}{8}\right\}h(r)-\tfrac{1}{3}y_1(2p,1s|r)1s(r)=0, \quad (15)$$

$$\left\{-\frac{1}{2}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{2}{r^2}\right)-\frac{1}{r}+\frac{1}{8}\right\}\theta(r)+\tfrac{1}{3}y_1(1s,2p|r)1s(r)+y_0(1s,1s|r)2p(r)-(1705/6561)2p(r)=0, \quad (16)$$

and

$$\left\{-\frac{1}{2}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{2}{r^2}\right)-\frac{1}{r}+\frac{1}{8}\right\}\phi(r)+\tfrac{1}{3}y_1(1s,2p|r)1s(r)-y_0(1s,1s|r)2p(r)+(1481/6561)2p(r)=0. \quad (17)$$

The solutions $g(r)$, $\theta(r)$, and $\phi(r)$ are linear combinations of the first-order Hartree-Fock (HF) orbitals, listed by Cohen.[2] The matrix elements can be evaluated analytically, and we obtain

$$(1s2p|g2p)_0=\frac{3512503}{3^6\times 10^5}+\frac{23}{81}\ln\frac{5}{6}=-0.0035878357,$$

$$(2p1s|g2p)_1=\frac{85638229}{3^8\times 5^4\times 7^2\times 10}+\frac{14}{729}\ln\frac{6}{7}+\frac{50}{729}\ln\frac{5}{7}=0.0165827681,$$

$$(1s1s|\theta 2p)_1=\frac{-15491589248}{3^{16}\times 5^3\times 7^2}+\frac{1}{3^{15}}(6291456\ln 2-116032\ln 3+1431200\ln 5-3470336\ln 7)=-0.0738163180,$$

$$(2p1s|\theta 1s)_0=\frac{-1178867542}{3^{13}\times 5^3\times 7^2}+\frac{1}{2\times 3^{13}}\times(3626\ln 3-14336\ln 7+12523\ln 5)=-0.1218994986,$$

and

$$(2p1s|\phi 1s)_0=\frac{20114286182}{3^{13}\times 5^5\times 7^2}+\frac{1}{2\times 3^{13}}\times(9877\ln 5+8918\ln 3-14336\ln 7)=0.0817006367.$$

To solve (15) for $h(r)$, we expanded according to

$$h(r)=\sum_{j=3}^{\infty} a_jL_j^3(2\beta r)r\exp(-\beta r), \quad (18)$$

with $\beta=\frac{1}{2}\sqrt{7}$. Then

$$(1s1s|h2p)_1=\frac{2^{18}}{3^{10}}\sum_{j=3}^{\infty}\frac{1}{j(j-1)(j-2)}\frac{1}{(j\beta-1-\beta)}J_j^2, \quad (19)$$

where

$$\begin{aligned}J_j={}&(j-2)\frac{(1+\beta)}{2\beta}\left(\frac{1-\beta}{1+\beta}\right)^j-\frac{j(1+\beta)}{2\beta}\left(\frac{1-\beta}{1+\beta}\right)^{j-1}\\&-(j-2)\frac{(5+2\beta)}{4\beta}\left(\frac{5-2\beta}{5+2\beta}\right)^j+\frac{j(5+2\beta)}{4\beta}\left(\frac{5-2\beta}{5+2\beta}\right)^{j-1}\\&-\frac{3}{4\beta}\left\{j(j-1)\left(\frac{5-2\beta}{5+2\beta}\right)^{j-2}-2j(j-2)\left(\frac{5-2\beta}{5+2\beta}\right)^{j-1}\right.\\&\left.+(j-1)(j-2)\left(\frac{5-2\beta}{5+2\beta}\right)^j\right\}+\frac{9}{32\beta^2}j(j-1)(j-2)\\&\times\left(\frac{4\beta}{5+2\beta}\right)^4\left(\frac{5-2\beta}{5+2\beta}\right)^{j-3}-\frac{27}{512\beta^3}j(j-1)(j-2)\\&\times\left(j+1-\frac{5+2\beta}{\beta}\right)\left(\frac{4\beta}{5+2\beta}\right)^6\left(\frac{5-2\beta}{5+2\beta}\right)^{j-4},\end{aligned} \quad (20)$$

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[2] M. Cohen, Proc. Phys. Soc. (London) 82, 778 (1963).

negative powers being excluded. The series (18) is rapidly convergent, and the dispersion term has the magnitude

$$(1s1s|h2p)=+0.0084131502.$$

Finally, using[3]

$$E_2(1s^2\,{}^1S)=-0.157666405,$$
$$E_2(1s2p\,{}^1P)=-0.15702294,$$
$$E_2(1s2p\,{}^3P)=-0.07299739,$$

we obtain

$$E_2(1s^22p\,{}^2P)=-0.52717136,$$

to which the pair energies contribute -0.34567396 and the nonadditive terms -0.18149740. The theoretical value is in harmony with the semiempirical value of -0.529, which we derive from an analysis of the exact nonrelativistic energies tabulated by Weiss.[4]

3. DISCUSSION

To second order the nonrelativistic eigenvalue of the $(1s^22p\,{}^2P)$ states is given by

$$E(Z)=-1.125Z^2+1.09352614Z-0.52717136\text{ a.u.}\quad(21)$$

and the HF eigenvalue is given by[5]

$$E^{\mathrm{HF}}(Z)=-1.125Z^2+1.093526Z-0.469462\text{ a.u.}\quad(22)$$

Thus, the correlation energy tends to a constant value of -0.057709 a. u. or -1.57 eV as the nuclear charge increases. The correlation energy of the helium $1s^2\,{}^1S$ sequence tends to a constant value of -1.27 eV[6], so that the addition of a $2p$ electron increases the correlation energy by 0.30 eV compared to the increase of 0.19 eV found for a $2s$ electron.[1]

As for the $1s^22s\,{}^2S$ states, most of the correlation energy arises from the pair energies. Thus, if we write

$$E_2^{\mathrm{HF}}(1s^22p\,{}^2P)=E_2^{\mathrm{HF}}(1s^2\,{}^1S)+\tfrac{1}{2}E_2^{\mathrm{HF}}(1s2p\,{}^1P)+\tfrac{3}{2}E_2^{\mathrm{HF}}(1s2p\,{}^3P)+\zeta^{\mathrm{HF}},\quad(23)$$

$\zeta-\zeta_{\mathrm{HF}}=0.001852$ a. u. $=0.050$ eV, while the contribution from the pair energies is -0.059561 a. u. $=-1.62$ eV. The comparable values for the $1s^22s^2S$ states are 0.001682 a. u. $=0.046$ eV and -0.055281 a. u. $=1.50$ eV.

TABLE I. Nonrelativistic binding energies of the $1s^22p\,{}^2P$ states (in a.u.).

Z	Measured	Hartree-Fock	Multi-configuration	Eq. (21)
3	7.41016	7.36507	7.40838	7.37159
4	14.17932	14.13085	14.17466	14.15307
5	23.20442	23.15370	23.19936	23.18454
6	34.48193	34.42986	34.47597	34.46605
7	48.01055	47.95775	48.00411	47.99749
8	63.78971	63.73666	63.78314	63.77896

Table I compares the results of Eq. (21) with the nonrelativistic eigenvalues derived by Weiss[4] from spectroscopic data, from HF calculations, and from 45-term multiconfiguration variational calculations. Equation (21) is superior to the HF approximation for $Z\geq3$, but the higher-order terms in the Z expansion remain sufficiently important that (21) is not more accurate than the 45-term multiconfiguration calculation until Z exceeds about 10. It appears that $E_3(Z)$ must be about $-0.07/Z$.

Taken in conjunction with the results for the $1s^22s\,{}^2S$ states, Eq. (21) gives for the nonrelativistic energies of the $1s^22p\,{}^2P-1s^22s\,{}^2S$ transition

$$\Delta E(Z)=0.07072093Z-0.11902237+O(Z^{-1})\text{ a. u.}\quad(24)$$

The HF approximation gives

$$\Delta^{\mathrm{HF}}E(Z)=0.07072093Z-0.114913+O(Z^{-1})\text{ a. u.,}\quad(25)$$

showing that a large cancellation of error occurs in the prediction of the transition energies.

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