

氮分子第一正带系振子强度的理论计算

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提 要

将前文^[1]提出的选择组态函数的准则从双电子激发扩充到三电子激发;采用投影算符消除其它多重态的影响;根据组态互作用法计算了氮分子第一正带系的振子强度,其值为0.00198,与实验完全吻合。

1. 选择组态函数的准则

前文^[1]提出了一套选择组态函数的准则,对于某些激发态,利用这套准则所能选择的组态函数过少。为了提高计算精度而又不过多地增加计算量,可将准则进一步扩充,即选择的组态函数除了前文提出的两部分外,增加第三部分如下:从轨道能大于 ϵ_g 的所有基态轨道上能得到自旋分量为 $s, s-1, \dots, -s$,轨道角动量在分子轴方向的投影量子数为 A 的三电子激发组态函数。而且,这些组态必须满足分子自旋算符 \hat{s}^2 和 \hat{s}_z 的本征方程。

2. 计算及结果

(1) 氮分子 $B^3\Pi_g$ 态的能量 $E(B^3\Pi_g)$ 及波函数 $X(B^3\Pi_g)$ ^[1]

$$E(B^3\Pi_g) = -108.29608 \text{ a.u.} \quad (1)$$

$$\left. \begin{aligned} X_1(B^3\Pi_g) &= B_1\phi_1(r) + B_2\phi_3(r) + B_3\phi_5(r) + B_4\phi_7(r) \\ X_2(B^3\Pi_g) &= B_1\phi_2(r) + B_2\phi_4(r) + B_3\phi_6(r) + B_4\phi_8(r) \end{aligned} \right\} \quad (2)$$

式中 $B_1=0.99939$, $B_2=-0.00352$, $B_3=-0.03478$, $B_4=-0.00033$ 。

(2) 氮分子 $A^3\Sigma_u^+$ 态的能态 $E(A^3\Sigma_u^+)$ 及波函数 $X(A^3\Sigma_u^+)$

按照扩充了的选择组态函数的准则,可得如下组态函数

$$\left. \begin{aligned} \phi_1(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_5\bar{\varphi}_5 \bar{\varphi}_6\bar{\varphi}_6 \bar{\varphi}_7\bar{\varphi}_7\| \\ \phi_2(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_5\bar{\varphi}_8 \bar{\varphi}_6\bar{\varphi}_6 \bar{\varphi}_7\bar{\varphi}_7\| \\ \phi_3(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_5\bar{\varphi}_5 \bar{\varphi}_6\bar{\varphi}_6 \bar{\varphi}_7\bar{\varphi}_{10}\| \\ \phi_4(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_{10} \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_5\bar{\varphi}_5 \bar{\varphi}_6\bar{\varphi}_6 \bar{\varphi}_7\bar{\varphi}_7\| \\ \phi_5(r) &= \|\bar{\varphi}_1\bar{\varphi}_{10} \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_5\bar{\varphi}_5 \bar{\varphi}_6\bar{\varphi}_6 \bar{\varphi}_7\bar{\varphi}_7\| \\ \phi_6(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_7\bar{\varphi}_7 \bar{\varphi}_8\bar{\varphi}_8 \bar{\varphi}_6\bar{\varphi}_6\| \\ \phi_7(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_3\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_7\bar{\varphi}_7 \bar{\varphi}_9\bar{\varphi}_9 \bar{\varphi}_5\bar{\varphi}_8\| \\ \phi_8(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_7\bar{\varphi}_7 \bar{\varphi}_{10}\bar{\varphi}_{10} \bar{\varphi}_6\bar{\varphi}_6\| \\ \phi_9(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_7\bar{\varphi}_7 \bar{\varphi}_{10}\bar{\varphi}_{10} \bar{\varphi}_5\bar{\varphi}_8\| \\ \phi_{10}(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_6\bar{\varphi}_6 \bar{\varphi}_8\bar{\varphi}_8 \bar{\varphi}_7\bar{\varphi}_{10}\| \\ \phi_{11}(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_6\bar{\varphi}_6 \bar{\varphi}_9\bar{\varphi}_9 \bar{\varphi}_7\bar{\varphi}_{10}\| \end{aligned} \right\} \quad (3)$$

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$$\begin{aligned}\phi_{12}(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_5\bar{\varphi}_5 \bar{\varphi}_8\bar{\varphi}_8 \bar{\varphi}_7\bar{\varphi}_{10}\| \\ \phi_{13}(r) &= \|\bar{\varphi}_1\bar{\varphi}_1 \bar{\varphi}_2\bar{\varphi}_2 \bar{\varphi}_3\bar{\varphi}_3 \bar{\varphi}_4\bar{\varphi}_4 \bar{\varphi}_5\bar{\varphi}_5 \bar{\varphi}_9\bar{\varphi}_9 \bar{\varphi}_7\bar{\varphi}_{10}\|\end{aligned}$$

将(3)式代入久期方程, 可得

$$E(A^3\Sigma_u^+) = -108.38010 \text{ a.u.} \quad (4)$$

$$\begin{aligned}X(A^3\Sigma_u^+) &= A_1\phi_1(r) + A_2\phi_2(r) + A_3\phi_3(r) + A_4\phi_4(r) + A_5\phi_5(r) \\ &+ A_6\phi_6(r) + A_7\phi_7(r) + A_8\phi_8(r) + A_9\phi_9(r) + A_{10}\phi_{10}(r) \\ &+ A_{11}\phi_{11}(r) + A_{12}\phi_{12}(r) + A_{13}\phi_{13}(r),\end{aligned} \quad (5)$$

式中

$$\begin{aligned}A_1 &= 0.69117 & A_2 &= 0.69117 & A_3 &= 0.00097 & A_4 &= 0.05204 \\ A_5 &= 0.00096 & A_6 &= -0.14446 & A_7 &= -0.14446 & A_8 &= -0.00738 \\ A_9 &= -0.00738 & A_{10} &= -0.00180 & A_{11} &= 0.00002 & A_{12} &= 0.00002 \\ A_{13} &= -0.00180\end{aligned}$$

于是, $B^3\Pi_g - A^3\Sigma_u^+$ 的振子强度为

$$f_{el} = 0.00198$$

3. 讨论

本文的理论计算值与实验值的比较见下表:

f_{el}	0.0028 ± 0.00098	0.002	0.00171	0.0028 ± 0.0007	0.00198
作者	А. П. Дронов ^[2]	M. Jeunehomme ^[3]	A. B. F. Duncan ^[4]	W. H. Wurster ^[5]	本文

计算值与 А. П. Дронов 等人的实验值完全吻合。表明本文提出的选择组态函数的准则既能保证较高的计算精度, 又能将计算量限制在一定范围内, 这在实际计算中是十分有用的。按照前文^[1]的准则, 有时只能得到单电子激发组态函数, 这样就必须采用本文的准则, 才能保证所需的计算精度。此外, 当基函数较多时, 这样做显得特别重要。

参 考 文 献

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Theoretic calculation of the oscillator strength of the first positive bands system of the nitrogen molecule

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Abstract

The set of criteria for selecting configuration function, presented in the previous paper^[2], are extended from double-electron excitation to three-electron excitation. The effect of other multiplicate states on the excited $B^3\Pi_g$ and $A^3\Sigma_u^+$ states are excluded by using the projection operator. By means of CI method the oscillator strength of the first positive band system of N_2 is calculated. The calculated value is 0.00198, being in good agreement with experimental values.