Theoret. chim. Acta (Berl.) 3, 159—163 (1965)

Department of Physical Chemistry, The University of Copenhagen, Copenhagen

A Calculation of the Spin-Orbit Splitting of the $X\ ^2\Pi$ State of NO

By

Ole J. Heilmann and **C. J. Ballhausen**

Using Brion, Moser and Yamazaki's SCF LCAO MO the spin orbit splitting of the $X\ ^2\Pi$ state of NO has been calculated using various potentials. Experimentally $W\ (^2\Pi_{3/2}) - W(^2\Pi_{1/2})$ is known to be 122 cm^{-1}. Using an "unscreened" nuclear field we find a value of 328 cm^{-1}. Inclusion of screening due to electronic repulsions reduces this value to 283 cm^{-1}. Agreement with the experimental value may be obtained by reducing the orbital exponents in the 2π molecular orbital by 30% over the value given by Slater's rules.

Die Spin-Bahn-Aufspaltung des $X\ ^2\Pi$-Zustandes von NO wurde mit verschiedenen Potentialen unter Verwendung der SCF LCAO MOs von Brion, Moser und Yamazaki berechnet. Der experimentelle Wert für $W\ (^2\Pi_{3/2}) - W\ (^2\Pi_{1/2})$ beträgt 122 cm^{-1}. Die Rechnung mittels eines reinen Kernfeldes liefert den Wert 328 cm^{-1} und unter Einschluß der Abschirmung durch die Elektronen 283 cm^{-1}. Übereinstimmung mit dem experimentellen Wert läßt sich erzielen, wenn man den Exponenten des 2π-Zustandes 30% kleiner als nach den Slater Regeln macht.

Avec les orbitals moléculaires SCF LCAO de Brion, Moser et Yamazaki, nous avons calculé le dédoublement spin-orbitale de l'etat $X\ ^2\Pi$ de NO. La valeur expérimentale $W\ (^2\Pi_{3/2}) - W\ (^2\Pi_{1/2})$ est 122 cm^{-1}. Dans un champ nucléaire «sans écran» on trouve 328 cm^{-1}. L'inclusion de l'effet d'écran dû aux répulsions interélectroniques réduit cette valeur à 283 cm^{-1}. La valeur expérimentale s'obtient, si l'on réduit de 30% les exposants d'après Slater dans l'orbitale moléculaire 2π.

Introduction

As is well known, the ground state of the NO molecule $X\ ^2\Pi$, exhibits a spin-orbit coupling, the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states being separated [2] by 122.094 cm^{-1}. In what follows we shall briefly report a perturbation calculation of this splitting, using the SCF LCAO MO given by Brion, Moser and Yamazaki [1]. A similar calculation using the same orbitals has apparently been performed by Lin, Hijikata and Sakamoto [3]. However, the very shortness of their report makes it difficult to see how they obtain their result of a 146 cm^{-1} splitting, and for this reason we have undertaken a similar investigation.

The Formalism

As our perturbation term for the spin-orbit energy we take [7]

$$\mathscr{H}^{(1)} = \sum_j \frac{1}{2\,m^2c^2}\ \hat{s}_j \cdot (\text{grad}\ V_j) \times \hat{p}_j \tag{1}$$

where the symbols have their usual meaning, and the summation extends over all the electrons in the molecule. We have here lumped together, in the potential V_j, the influence of all the other nuclei and electrons on electron number j.

Changing to cylindrical coordinates [6] (ϱ, φ, z) which is convenient for an electron moving in the field of two nuclei [4] we rewrite $\mathscr{H}^{(1)}$ as

$$\mathscr{H}^{(1)}_j = \frac{\hbar}{2\,i m^2 c^2}\left[e^{-i\varphi_j}\,(\hat{A}_j - i\hat{B}_j)\,\hat{s}_{+j} + e^{i\varphi_j}\,(\hat{A}_j + i\hat{B}_j)\,\hat{s}_{-j} + \hat{C}_j\,\hat{s}_{zj}\right] \tag{2}$$

$$\hat{A}_j = \frac{1}{2}\left[\frac{\partial V_j}{\varrho_j\,\partial\varphi_j}\frac{\partial}{\partial z_j} - \frac{\partial V_j}{\partial z_j}\frac{\partial}{\varrho_j\,\partial\varphi_j}\right] \tag{3}$$

$$\hat{B}_j = \frac{1}{2}\left[\frac{\partial V_j}{\partial z_j}\frac{\partial}{\partial\varrho_j} - \frac{\partial V_j}{\partial\varrho_j}\frac{\partial}{\partial z_j}\right] \tag{4}$$

$$\hat{C}_j = \left[\frac{\partial V_j}{\partial\varrho_j}\frac{\partial}{\varrho_j\,\partial\varphi_j} - \frac{\partial V_j}{\varrho_j\,\partial\varphi_j}\frac{\partial}{\partial\varrho_j}\right] \tag{5}$$

For the potential in which electron j moves we take

$$V_j = \sum_{\text{nuc}} V_{\text{nuc}}\,(\varrho_j, Z_j) + \sum_{j\neq i}\frac{e^2}{r_{ij}}\,. \tag{6}$$

Let us designate our wavefunctions by $(n\Lambda SM_\Lambda\,M_S)$ where $\Lambda = 0, 1, 2\cdots$ is the cylindrical quantum number. In cylindrical symmetry we have as usual that $M_\Lambda + M_S$ is a good quantum number. The first two terms, in the perturbation operator, will therefore mix wavefunctions with $\Delta M_\Lambda = 1$. Since, in our approximation, we will not consider off diagonal terms in the electronic energy, we take

$$\mathscr{H}^{(1)} = \sum_j \frac{\hbar}{2\,i m^2 c^2}\left[\frac{\partial V_j}{\partial\varrho_j}\frac{\partial}{\varrho_j\,\partial\varphi_j} - \frac{\partial V_j}{\varrho_j\,\partial\varphi_j}\right]\hat{s}_{zj} \tag{7}$$

and because in cylindrical symmetry V_j does not depend upon φ_j, equation (7) reduces to

$$\mathscr{H}^{(1)} = \sum_j \frac{\hbar}{2\,i m^2 c^2}\left[\frac{\partial V_j}{\varrho_j\,\partial\varrho_j}\frac{\partial}{\partial\varphi_j}\right]\hat{s}_{zj}\,. \tag{8}$$

With

$$-i\hbar\frac{\partial}{\partial\varphi} = \hat{l}_z$$

we get

$$\mathscr{H}^{(1)} = \sum_j \frac{1}{2\,m^2 c^2}\left[\frac{1}{\varrho_j}\frac{\partial V_j}{\partial\varrho_j}\right]\hat{l}_{zj}\cdot\hat{s}_{zj}\,. \tag{9}$$

The spin-orbit coupling in linear molecules can then be expressed as $D\cdot M_\Lambda\cdot M_S$, and D can be evaluated in a manner similar to that used for the atomic case.

Instead of working with the above expression (7), it is sometimes convenient to transform the operator so that instead of the derivatives of the potential it is the potential itself which appears in the operator. One way of obtaining this is by means of partial integration, since the integrated parts vanish at the limits. In this way we get the matrix element

$$\begin{aligned}&(n\Lambda\,SM_\Lambda\,M_S\,|\mathscr{H}^{(1)}\,|\,n\Lambda\,SM_\Lambda\,M_S)\\ &= \frac{\hbar}{m^2c^2}M_S\int\left(\frac{1}{\varrho_j}\frac{\partial}{i\,\partial\varphi_j}\psi^*\right)V_j\left(\frac{\partial}{\partial\varrho_j}\psi\right)d\tau\end{aligned} \tag{10}$$

where the integration runs over all electronic coordinates. This is as far as we can go without specifying ψ.

Let us now suppose that ψ is given as a Slater determinant. Since the spin-orbit operator, as here defined, is a one electron operator, we see that in using

Slater determinants as wavefunctions we must leave out the socalled exchange terms in the diagonal elements.

Consider a Slater wavefunction made up of N electrons where N-1 electrons are in closed shells with one electron outside the closed shells. The wavefunction for this electron, ψ_N, is characterized by having $m_\lambda \neq 0$ and α spin. The other single electronic functions are called ψ_i $(i = 1, 2 \cdots N - 1)$. Then taking for V_N

$$V_N = V(\varrho_N, Z_N) + \sum_{i \neq N} \frac{e^2}{r_{iN}} \tag{11}$$

we get

$$(n\Lambda\, S M_\Lambda\, M_S\, | \mathscr{H}^{(1)} |\, n\Lambda\, S M_\Lambda\, M_S)$$

$$= -\frac{\hbar^2}{2\,m^2\,c^2}\, m_\lambda \left[\int d\tau_N\, \psi_N^* \frac{1}{\varrho_N} V_N(\varrho_N Z_N) \frac{\partial\, \psi_N}{\partial\, \varrho_N} + \right.$$

$$\left. + \sum_{i \neq N} e^2 \int d\tau_N \int d\tau_i\, \psi_N^* \frac{1}{\varrho_N} \frac{\partial \psi_N}{\partial \varrho_N} \frac{1}{\varrho_{iN}} \psi_i^* \psi_i \right] \tag{12}$$

Splitting of $X\,^2\Pi$ in NO

The ground electronic state $^2\Pi$ with $M_\Lambda = 1$ and $M_S = +1/2$ can be represented by a single determinant [1]

$$|\,(1\,\sigma)^2\,(2\,\sigma)^2\,(3\,\sigma)^2\,(4\,\sigma)^2\,(5\,\sigma)^2\,(1\,\pi)^4\,(2\,\pi^{\alpha+})\,|\ . \tag{13}$$

Let us first use eq. (9) to calculate the splitting. We then get

$$W(^2\Pi_{3/2}) - W(^2\Pi_{1/2}) = \frac{\hbar^2}{2\,m^2\,c^2} \int (2\,\pi^+)^* \frac{1}{\varrho} \frac{\partial V}{\partial \varrho} (2\,\pi^+)\, d\tau\ . \tag{14}$$

From Brion, Moser and Yamazaki we have

$$(2\,\pi^+) = 0.8781\ 2p\pi_{\mathrm{N}} - 0.6939\ 2p\pi_{\mathrm{O}}\ . \tag{15}$$

This wave function is normalized including overlap and the 2 p functions are Slater orbitals

$$2p\pi = \sqrt{\frac{Z^5}{2\,\pi}}\, r \sin\theta\, e^{i\varphi}\, e^{-Zr/2} \tag{16}$$

having $Z_{\mathrm{N}} = 3.90$ and $Z_{\mathrm{O}} = 4.55$.

Firstly we make a simplified calculation using a screened potential and assuming the zero differential overlap approximation putting $(2p\pi_{\mathrm{N}})$ $(2p\pi_{\mathrm{O}})$ equal to zero. In renormalizing, we then divide $(2\,\pi^+)$ with 1.1190. Close to the N and O nuclei, where $\frac{1}{\varrho}\frac{\partial V}{\partial \varrho}$ is large, we assume that the potential equals the atomic potential. Since in that case the integrals reduce to the atomic $\zeta_{n,l}$ expressions, we get

$$\Delta W = 0.6158\, \zeta\,(\mathrm{N}) + 0.3842\, \zeta\,(\mathrm{O})\ . \tag{17}$$

From Moore's [5] tables we get ζ O $(I) = 147$ cm^{-1} and extrapolate ζ N $(I) =$ 64 cm^{-1}. Hence $\Delta W = 96$ cm^{-1}.

Had we, on the other hand, performed the integrations with $V_j = -\frac{Z'_{\mathrm{O}}\, e^2}{r_{j\mathrm{O}}} - \frac{Z'_{\mathrm{N}}\, e^2}{r_{j\mathrm{N}}}$ we would have obtained ΔW (cm^{-1}) $= 8.902\, Z'_{\mathrm{N}} + 8.820\, Z'_{\mathrm{O}}$. With $Z'_{\mathrm{N}} = 3.90$ and $Z'_{\mathrm{O}} = 4.55$ we obtain $\Delta W = 75$ cm^{-1}.

Dropping the zero differential overlap approximation we get two more contributions to the unscreened value of $\Delta W = 166\ \text{cm}^{-1}$. The first arises when one considers the one center integrals in the product expansion of $\psi_N^* \frac{1}{\varrho_N} \frac{\partial \psi_N}{\partial \varrho_N}$, the second from the true two center integrals in the same expansion. The values of the integrals are, using unscreened values of Z' and including the overlap in the normalization, $\Delta W' = 176\ \text{cm}^{-1}$ and $\Delta W'' = -14\ \text{cm}^{-1}$. The total effect of only considering the field from the nuclei is then a splitting of $166 + 162 = 328\ \text{cm}^{-1}$.

The inclusion of the field from the other 14 electrons, as expressed in the second term of eq. (12), produces a screening effect of $\Delta W_{\text{elec}} = -45\ \text{cm}^{-1}$. The final result is thus a spin-orbit splitting $^2\Pi_{3/2} - {}^2\Pi_{1/2} = 283\ \text{cm}^{-1}$.

Discussion

The reason that the calculated value of $283\ \text{cm}^{-1}$ is in bad agreement with the experimental value of $122\ \text{cm}^{-1}$ is presumably that the used molecular orbitals utilizing $2p$ atomic orbitals all have the same "effective" charge. In other words, the orbital exponents for the antibonding uppermost $(2\pi^+)$ molecular orbital are the same as for the (1π) and the (3σ) (4σ) and (5σ) molecular orbitals. Of the "screening effect" of $45\ \text{cm}^{-1}$, we find that $33\ \text{cm}^{-1}$ comes from the four electrons in (1σ) and (2σ) molecular orbitals that are nearly identical with the atomic $(1s)$ orbitals. The next 10 electrons produce only a "screening effect" of $12\ \text{cm}^{-1}$.

In order to investigate whether this explanation is reasonable we have put a variable parameter c into the 2π molecular orbital

$$\varphi_{2\pi} = a_{\text{N}}\,(2p\pi_{\text{N}}) + a_{\text{O}}\,(2p\pi_{\text{O}}) \tag{18}$$

$$(2p\pi) = \sqrt{\frac{(cZ)^5}{2\pi}}\, r e^{-\frac{cZr}{2}} \sin\theta\, e^{i\varphi} \tag{19}$$

where a_{N} and a_{O} are fixed in such a way that $\varphi_{2\pi}$ is kept normalized and orthogonal upon $\varphi_{1\pi}$. The whole calculation with all terms included was then repeated. The results are given in the table.

Table. *Spin-orbit splitting of $^2\Pi$ as a function of the screening parameter c*

c	$W(^2\Pi_{3/2}) - W(^2\Pi_{1/2})$
1.00	$283\ \text{cm}^{-1}$
0.90	$219\ \text{cm}^{-1}$
0.80	$165\ \text{cm}^{-1}$
0.70	$121\ \text{cm}^{-1}$
0.60	$85\ \text{cm}^{-1}$

The experimental value of the spin-orbit splitting is seen to correspond to $c \simeq 0.70$, leading to a 30% reduction of the effective charge on the $2p\pi$ orbitals of Z_{N} from 3.90 to 2.73 and of Z_{O} from 4.55 to 3.18.

Finally it is worth noticing that, with overlap included in the normalization of the wavefunction for $(2\pi^+)$ and using the zero differential overlap approximation and the experimental values of $\zeta_{n,l}$, we get a $\Delta W = 120\ \text{cm}^{-1}$. However, this is probably only a fortunate accident, since, by dropping the zero differential overlap approximation, ΔW becomes larger than the experimental value by a factor of three. As usual the most naive calculation thus produces the best numerical result.

Evaluation of the Integrals

All of the integrals were evaluated on the GIER computer located at the H. C. Ørsted Institute. The two center integrals occuring with the simple screened potential were calculated either in spherical – or elliptic coordinates by Gauss-quadratur. The integrals occuring when the electronic screening terms are included were calculated by Gauss-quadratur using an ALGOL program "TECRIB open".

References

[*1*] Brion, H., C. Moser, and Y. Yamazaki: J. chem. Physics **30**, 673 (1959).
[*2*] Favero, P. G., A. M. Mirri, and W. Gordy: Physic. Rev. **114**, 1534 (1959).
[*3*] Lin, C. C., K. Hijikata, and M. Sakamoto: J. chem. Physics **33**, 878 (1960).
[*4*] Mizushima, M., and S. Koide: J. chem. Physics **20**, 765 (1952).
[*5*] Moore, C.: Atomic Energy Levels, Vol. I, Washington: Circular of the National Bureau of Standards 467, 1949, p. 32.
[*6*] Pauling, L., and E. B. Wilson: Introduction to Quantum Mechanics. New York: McGraw Hill 1935, p. 443.
[*7*] Schiff, L. I.: Quantum Mechanics, New York: McGraw Hill 1955, p. 333.

(Received February 23, 1965)