

THEORETICAL STUDIES OF MOLECULAR IONS. VERTICAL IONIZATION POTENTIALS OF THE NITROGEN MOLECULE

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The $2\Sigma_g^+$, $2\Pi_u$, and $2\Sigma_u^+$ vertical ionization energies of nitrogen are obtained by using our theory of molecular electron affinities and ionization potentials, which permits the direct calculation of the ion-molecule energy differences. The contributions of charge redistribution and correlation energy change to the calculated ionization potentials are evaluated. The computational efficiency of the method is illustrated and comparisons are made with recent experimental results.

1. Introduction

In a previous publication [1], we developed a computationally tractable theory of molecular electron affinities and ionization potentials in which the ion-molecule energy difference is obtained directly rather than as a result of carrying out two separate variational calculations. Such a direct-calculation theory permits us to effect a formal cancellation of those terms which contribute equally, through third order in perturbation theory, to the ion and molecule energies. The relationship of our equations-of-motion (EOM) technique to Rayleigh-Schrödinger (RS) perturbation theory and Green's function theory has been discussed by us in ref. [1] and elsewhere [2]. A most important point for understanding the results presented here is to recall from ref. [1] that the adjustment of the parent's Hartree-Fock molecular orbitals as well as the change in correlation energy which accompanies ionization are incorporated into our theory in a manner which allows the ion-molecule energy difference to be obtained accurately through third order in the electron interactions r_{ij}^{-1} . As described in ref. [3], we have successfully applied our EOM approach to the low-lying $2\Sigma^+$ and 2Π ionization potentials of hydrogen fluoride. The results of our

calculations in these cases were within 0.15 eV of the experimental photoionization measurements of Chupka et al. [4].

A principal purpose of the present paper is to present and analyze the results of applying our EOM method to the $X^1\Sigma^+ \rightarrow 2\Sigma_g^+$, $X^1\Sigma^+ \rightarrow 2\Sigma_u^+$ and $X^1\Sigma^+ \rightarrow 2\Pi_u$ vertical ionization energies of the nitrogen molecule. The experimental data on this molecule, which was obtained by photoionization [5] and photoelectron [6] spectroscopy, provides us with an excellent source of information with which to compare our theoretical predictions.

In section 2 the computational methods used to obtain the ionization energies are described briefly. Section 3 contains the results of our calculations as well as a discussion of their probable accuracy and our closing comments.

2. Description of the method

In our EOM theory of electron affinities and ionization potentials, the excitation operator Ω_μ , which generates the, in principle exact, eigenstate $|\mu^+\rangle$ of the positive ion when operating on the true neutral-molecule ground state $|g\rangle$,

$$\Omega_\mu |g\rangle = |\mu^+\rangle, \quad (1)$$

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is approximated in terms of the second-quantized Hartree-Fock orbital creation $\{C_i^+\}$ and annihilation $\{C_i\}$ operators as follows^{*}:

$$\Omega_\mu = \sum_i X_i(\mu) C_i + \sum_{m < n, \alpha} Y_{n\alpha m}(\mu) C_n C_\alpha^+ C_m + \sum_{\alpha < \beta, m} Y_{\alpha m \beta}(\mu) C_\alpha C_m^+ C_\beta. \quad (2)$$

The operator C_i^+ (C_i) creates (destroys) an electron in the Hartree-Fock spin-orbital ϕ_i . Greek indices α, β, γ label "occupied" Hartree-Fock spin-orbitals, m, n, p, q label "unoccupied" spin-orbitals, and i, j, k, l label either set. The $X_i(\mu)$, $Y_{n\alpha m}(\mu)$, and $Y_{\alpha m \beta}(\mu)$ are expansion coefficients which are determined by making use of the EOM theory of ref. [1] whose pertinent aspects are briefly reviewed below. An analogous expansion for the operator Ω_λ^+ which generates negative-ion eigenstates when operating on $|g\rangle$ is also given in ref. [1].

By assuming that $|g\rangle$ and $|\mu^+\rangle$ exactly obey the following Schrödinger equations

$$H|g\rangle = E|g\rangle, \quad (3a)$$

and

$$H|\mu^+\rangle = E_\mu^+ |\mu^+\rangle, \quad (3b)$$

one immediately obtains the basic equations of motion

$$[H, \Omega_\mu] |g\rangle = (E_\mu^+ - E) \Omega_\mu |g\rangle, \quad (3c)$$

which we have used to derive the following working matrix pseudo-eigenvalue problem involving the electron affinities or ionization potentials and the coefficients $X_i(\lambda)$, or $X_i(\mu)$:

$$\sum_j H_{ij}(\Delta E_\lambda) X_j(\lambda) = \Delta E_\lambda X_i(\lambda), \quad (4a)$$

or

$$\sum_j H_{ij}(\Delta E_\mu) X_j(\mu) = \Delta E_\mu X_i(\mu), \quad (4b)$$

where ΔE_λ is $E_\lambda^- - E$ and $\Delta E_\mu = E - E_\mu^+$. These results can be derived by using the approximation to Ω_μ given in eq. (2) or its electron-affinity analog and the RS approximation to $|g\rangle$

$$|g_{RS}\rangle = N_0^{-1/2} \left[|0\rangle + \sum_{m < n, \alpha < \beta} \frac{\langle mn|\alpha\beta\rangle}{\epsilon_\alpha + \epsilon_\beta - \epsilon_m - \epsilon_n} \times C_m^+ C_n^+ C_\beta C_\alpha |0\rangle \right] \quad (5)$$

in eq. (3c). The coefficients $Y_{n\alpha m}$ and $Y_{\alpha m \beta}$ have been eliminated by partitioning the resulting equations. In eq. (5), N_0 is a normalization constant, ϵ_i is the Hartree-Fock energy of spin-orbital ϕ_i , and the $\langle mn|\alpha\beta\rangle$ are antisymmetrized two-electron integrals over the spin-orbitals $\phi_m, \phi_n, \phi_\alpha$, and ϕ_β . The Hartree-Fock wavefunction of the neutral parent is represented by $|0\rangle$. The elements of the matrix $H_{ij}(\Delta E)$ are given in eq. (37) of ref. [1] as

$$H_{ij}(\Delta E) = A_{ij} + \sum_{\alpha < \beta, m} \frac{B_{i, \alpha m \beta} B_{j, \alpha m \beta}^*}{E_{\alpha\beta}^m + \Delta E} + \sum_{m < n, \alpha} \frac{B_{i, n \alpha m} B_{j, n \alpha m}^*}{-E_{\alpha}^{mn} + \Delta E}, \quad (1-37)$$

where ΔE is either ΔE_λ or ΔE_μ . The quantities appearing in this equation are defined in eqs. (31d)–(35) of ref. [1]. The physical significance of the terms in the above expression for $H_{ij}(\Delta E)$, which is discussed more completely in ref. [1], can be summarized for the case of ionization from ϕ_N as follows (analogous conclusions can be made for ionization from other orbitals):

(i) The $\beta = N$ terms in the first sum in eq. (1-37) contribute to the ion-neutral Hartree-Fock energy difference; therefore, these terms contain the effects of charge redistribution on the calculated ionization energies.

(ii) The second sum approximates the negative of the correlation energy of an electron in ϕ_N , which is vacant in the positive ion, interacting with all other electrons.

(iii) The $\beta \neq N$ terms in the first sum give the approximate change in correlation energy of the parent's N electrons caused by the removal of an electron from ϕ_N .

* For a good description of the properties of such Fermion creation and annihilation operators, see ref. [7].

To make use of eq. (4a) or eq. (4b), one must first carry out a Hartree-Fock calculation on the parent molecule of interest, after which the necessary[#] two-electron integrals must be transformed to the Hartree-Fock basis. In its present form, the theory is restricted, because[‡] of the use of eq. (5) for $|g\rangle$, to closed-shell parent molecules. This does not prohibit us from computing the electron affinity of, for example, the OH radical, however, because we can obtain the desired energy difference by calculating the ionization potential of the closed-shell species OH^- . Only those energy differences for which neither the ion nor the molecule are closed shell are presently outside the capability of our method. We are currently devoting considerable effort toward developing an extension of our EOM approach for use on such open-shell systems.

Once the Hartree-Fock orbital energies and two-electron integrals have been computed, the quantities A_{ij} , E_{α}^{mn} , $E_{\alpha\beta}^m$, $B_{i,n\alpha m}$, $B_{j,n\alpha m}$, and $B_{i,\alpha m\beta}$, $B_{j,\alpha m\beta}$, can be formed. This step is carried out only once; it is not part of the iterative procedure used to solve eq. (4a) or eq. (4b) which is described below. The fact that $\mathbf{H}(\Delta E)$ is block diagonalized by molecular symmetry allows us to compute only a limited set of the above-mentioned quantities, which leads to a very important savings in computation time. As an initial approximation to the desired ionization potential ΔE_{μ} or electron affinity ΔE_{λ} , one can choose the Koopmans' theorem [8] value

$$\Delta E \approx \epsilon_i, \quad (6)$$

for ionization from (or into) orbital ϕ_i . In this approximation, we assume that the state of the ion being studied is related, through zeroth order, to the parent's Hartree-Fock wavefunction by the addition or removal of an electron from a single spin-orbital. For the so-called shake up states^{††} of a positive ion,

[#] The molecular symmetry permits us to significantly reduce the complexity of our calculations. This simplification reduces the number of two-electron integrals which must be transformed to the Hartree-Fock basis.

^{*} If the parent molecule were open-shell, both single- and triple-excitations would also have to be included in $|g\rangle$.

^{††} Purvis and Öhrn [9] have carried out second-order ionization potential calculations on N_2 using propagator methods, which are very closely related to our EOM approach. In contrast to the present study, these workers investigated all of the ionization energies of N_2 , including the shake up processes, although they included only second-order terms in ΔE_{μ} .

in which ionization is accompanied by excitation of the ion, the initial estimate for ΔE_{μ} should be taken to be of the form $\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_p$, where the meaning of the subscripts was discussed earlier. Such states are not treated in our studies of the nitrogen molecule and will not be discussed further here. The fact that the Koopmans' theorem initial guess may be quite far (≥ 1 eV) from the correct ΔE leads one to inquire about the possibility of the iterative procedure converging to some ion-molecule energy difference other than the energy which is appropriate to the state of interest. Because the pseudo-eigenvalue problem expressed in eq. (4a) or eq. (4b) is symmetry-diagonalized, this problem will arise only if there exists a state whose symmetry is the same as that of the state of interest and whose ionization energy is close to the initial Koopmans' theorem estimate. In this uncommon situation, a more detailed analysis of the dependence of the solution to eq. (4a) or eq. (4b) upon the initial estimate for ΔE is required; in all of our calculations to date, such difficulties have not arisen.

Given the quantities appearing in eq. (1-37) and an initial approximation to ΔE , the matrix elements $H_{ij}(\Delta E)$ belonging to the proper symmetry block can be formed in a straightforward manner^{##}, as shown in eq. (1-37). The particular eigenvalue of $\mathbf{H}(\Delta E)$ which lies closest to the previous approximation to ΔE can then be used as the next approximation in forming a new $\mathbf{H}(\Delta E)$ matrix. This iterative solution of the working equations [eq. (4a) or (4b)] of our theory, in combination with Aiken's method [10] for improving the rate of convergence, has been successfully employed to generate the results presented below for the low-lying ionization energies of the nitrogen molecule as well as analogous ion-molecule energy differences for other interesting species, e.g., HF, OH^- , and BeH^- . Let us now turn to an analysis of our results on the low-lying ionization potentials of N_2 .

^{##} In forming the product $B_{i,n\alpha m} B_{j,n\alpha m}$, only the second- and third-order terms are kept. A fourth-order contribution, which arises from the product of the second-order components of $B_{i,n\alpha m}$ and $B_{j,n\alpha m}$, must not be included in the calculation.

Table 1

24-function Hartree-Fock wavefunction for N_2 . $R = 2.0680$ au, $E = -108.8644$ au, $\epsilon_{1\sigma_g} = -15.7511$, $\epsilon_{1\sigma_u} = -15.7475$, $\epsilon_{2\sigma_g} = -1.5614$, $\epsilon_{2\sigma_u} = -0.7994$, $\epsilon_{1\pi_u} = -0.6530$, $\epsilon_{3\sigma_g} = -0.6460$

σ atomic orbitals	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	π atomic orbitals	$1\pi_u$
N1s (5.9989)	0.5262	0.5274	-0.2184	-0.1799	-0.0446	N2p (1.4960)	0.4599
N2s (1.4147)	0.0009	-0.0030	0.0024	0.3606	0.3084	N2p' (3.2390)	0.1900
N2p (1.4960)	-0.0012	-0.0041	0.1345	-0.1496	-0.4050	N3d (2.4370)	0.0124
N1s' (8.5276)	0.1863	0.1867	0.0181	0.0078	-0.0075		
N2s' (2.2523)	-0.0001	-0.0011	0.5143	0.5056	0.1234		
N2p' (3.2390)	0.0034	0.0034	0.1473	-0.1064	-0.2372		

3. Results and discussion

Our calculations on the $1\Sigma_g^+ \rightarrow 2\Sigma_g^+$, $1\Sigma_g^+ \rightarrow 2\Pi_u$, and $1\Sigma_g^+ \rightarrow 2\Sigma_u^+$ ionization energies of N_2 were carried out within a twenty-two-function Slater type basis using a modification of Harris' DIATOM program to generate the necessary Hartree-Fock orbital energies and two-electron integrals. Table 1 contains information describing the basis set and the (restricted) Hartree-Fock orbital energies and molecular orbital expansion coefficients, for occupied orbitals.

For this basis, the iterative solution of eq. (4b) for vertical ($R = 2.0680$ au) ionization to the $2\Sigma_g^+$ state of N_2^+ converged to an approximate ionization energy of 15.69 eV, which is compared to the Koopmans' theorem prediction of 17.58 eV and the experimental result [5, 6] of 15.60 eV. Six minutes and fifty seconds of Univac 1108 computer time was required to calculate the Hartree-Fock orbital energies and the two-electron integrals in the Hartree-Fock basis; an additional fifty seconds was needed to compute the above ionization energy. The $2\Sigma_u^+$ ionization potential generated by our method is 18.63 eV, which compares favorably with the experimental measure-

ment [6] of 18.78 eV and is a significant improvement over the Koopmans' theorem prediction of 21.75 eV. Fifty seconds of time was required for this calculation, and for the computation of the $2\Pi_u$ ionization energy of N_2 . Our method predicts 17.03 eV for the $2\Pi_u$ vertical ionization potential which is in good agreement with the experimental result of 16.98 eV. In this case, the Koopmans' theorem ionization energy is 17.76 eV for our basis set. In table 2 we present our predicted ionization potentials along with those of Purvis and Öhrn [9] and the experimental results of ref. [6]. Although the basis set used in our work is not identical to that employed by Purvis and Öhrn, we feel that the differences between our ionization energies and the results of ref. [9] can be attributed primarily to the third order contributions to $H(\Delta E)$ which appear in our theory but which do not occur in the propagator method used in ref. [9].

By forming $H(\Delta E)$ using only the $\beta = N$ terms in the first sum in eq. (1-37), which generates our approximation to the ion-molecule Hartree-Fock energy difference, eq. (4b) yields 16.05 eV for the $2\Sigma_g^+$ ionization energy, 15.74 eV for the $2\Pi_u$ state, and 20.03 eV for the $2\Sigma_u^+$ ionization potential. These

Table 2
Summary of ionization potentials of nitrogen (in eV)

Ion state	Koopmans' theorem	$\Delta E_{HF}^a)$	EOM ^{b)}	Propagator [9]	Experiment [6]
$2\Sigma_g^+$	17.58	16.05	15.69	14.91	15.60
$2\Pi_u$	17.76	15.74	17.03	17.23	16.98
$2\Sigma_u^+$	21.75	20.03	18.63	17.55	18.78

a) Our approximate ion-molecule Hartree-Fock energy difference, which is computed by including only the $\beta = N$ terms in the first sum of eq. (1-37).

b) The present third-order EOM results.

predictions are in very good agreement with the Hartree-Fock energy differences obtained by Cade et al. [11] at $R = 2.0132$ au. The differences between these approximate Hartree-Fock results and our predictions obtained using the full $H(\Delta E)$ represent the contribution of electron correlation energy to the ionization potentials. A comparison of the Koopmans' theorem ionization potentials with the approximate Hartree-Fock predictions and the EOM results, which are summarized in table 2, leads to the conclusion that charge redistribution effects are the most important corrections to Koopmans' theorem for these specific ionization potentials. However, correlation energy effects must be included if one is interested in reaching an accuracy of better than ± 1.0 eV. To be of help to experimentalists who are studying ionization processes, any theoretical predictions should certainly be accurate to within 0.3 eV and, hopefully, to ± 0.15 eV. Thus, correlation energy must be properly treated to obtain theoretical results which are of significance.

Based upon our experience in these calculations on N_2 and with similar calculation on HF and other molecular systems, we believe that a further increase in the size of our basis set would not alter the above ionization energies by more than ± 0.05 eV. Furthermore, we feel that, for calculations in which a sufficiently large atomic orbital basis has been employed, the limitations which are inherent to the approximations used in our approach give rise to a probable precision of ± 0.15 eV. As can be seen from table 2, our calculated ionization potentials agree with the experimental measurements of ref. [6] to within the estimated limits of our theory. The results of our calculations on HF which have been reported elsewhere [3], also indicate that our method is capable of yielding ion-molecule energy differences to within 0.15 eV. Although such uncertainties are much larger than the limits of reproducibility which are common to photoionization and photoelectron measurements (± 0.01 eV), the difficulties associated with interpreting experimental threshold data[†] makes the ex-

traction of a vertical ion-molecule electronic energy difference from such data a procedure whose precision limits are often of the order of ± 0.1 eV. Thus, the results of our calculations on molecules and ions of chemical importance should be of much use and interest to experimentalists who are studying photoionization, photodetachment, and photoelectron spectroscopy.

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[†] For an excellent discussion of the techniques used to deconvolute experimental photoionization data, see ref. [12].