# Transition moments between excited electronic states of N2

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# Transition moments between excited electronic states of $N_2$*

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We report the transition moments between the excited states of molecular nitrogen including their dependence on internuclear distance. These moments are calculated using the equations of motion method and can be obtained with only a slight increase in the effort needed to obtain the ground to excited state transition moments. The transition moments along with reliable vibrational wavefunctions should be useful in the analysis of observed band intensities of $N_2$.

## I. INTRODUCTION

Recently we have derived expressions for the transition moment between excited states which are consistent with the approximations and assumptions normally used to obtain transition moments between the ground and excited states in the equations of motion method.[1] This can be a useful result since the method has already been shown to yield reliable transition moments between the ground and excited states of molecules.[2] Excited state–excited state transition moments are needed in the analysis of several systems. For example, the first positive band of $N_2(B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+)$ gives one of the major contributions to the radiation from hot air in the visible and near infrared at temperatures up to $10^4$ K and is a strong emitter in auroral displays. Excited state–excited state electronic transition moments and their dependence on internuclear distance are needed to explain and predict these band intensities. Transition moments between excited states can also be important in the modeling of gas phase layers, e.g., the $C\,^3\Pi_u \rightarrow B\,^2\Pi_g$ lasing transition in $N_2$.

In this paper we report transition moments and their dependence on internuclear distance for a large number of transitions between excited states of $N_2$. These include the following band systems: $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ (first positive system), $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ (second positive system), $B'\,^3\Sigma_u^- \rightarrow B\,^3\Pi_g$ (infrared afterglow system), $B\,^3\Pi_g \rightarrow W\,^3\Delta_u$, $a\,^1\Pi_g \rightarrow W\,^1\Delta_u$, $a\,^1\Pi_g \rightarrow a'\,^1\Sigma_u^-$, and $a\,^1\Pi_g \rightarrow b\,^1\Pi_u$. We also report transition moments between the $a\,^1\Pi_g$ state and the more complex $^1\Sigma_u^+$ states. These excited state–excited state transition moments are calculated directly from the set of ground state–excited state transition densities obtained from a single equations-of-motion calculation on the $^1\Sigma_g$ ground state of $N_2$. In the next section we briefly outline the results of Ref. 1 which define the excited state–excited state transition moments. We then present the results for many band systems of $N_2$ at six internuclear distances between $R = 0.90$ Å and $R = 1.4$ Å. The values are given in Tables I and II.

## II. THEORY

In the equations-of-motion (EOM) method as well as in several many-body methods, e.g., in the theory of Green's functions, one calculates relative quantities such as transition energies and densities directly. The transition energies and transition densities are sufficient to evaluate the physically significant matrix elements of interest in spectroscopy. For example, the matrix element of a one-particle operator $M$ between the ground state $|0\rangle$ and an excited state $|\lambda\rangle$ can be written

$$\langle 0|M|\lambda\rangle = \int d^3\mathbf{r} d^3\mathbf{r}' \delta(\mathbf{r}-\mathbf{r}') M(r) \rho_{0\lambda}(\mathbf{r},\mathbf{r}'), \tag{1}$$

where the one-particle transition density is given by

$$\rho_{0\lambda}(\mathbf{r}',\mathbf{r}) = \langle 0|\rho(\mathbf{r}',\mathbf{r})|\lambda\rangle. \tag{2}$$

In Eq. (2), $\rho(\mathbf{r}',\mathbf{r})$ is the one-particle density operator

$$\rho(\mathbf{r}',\mathbf{r}) = \hat{\psi}^+(\mathbf{r}')\hat{\psi}(\mathbf{r}) \tag{3}$$

in second quantized form with $\psi^+(\mathbf{r})$ and $\psi(\mathbf{r})$ the field operators, e.g.,

$$\hat{\psi}^+(\mathbf{r}) = \sum_k \phi_k^*(r) a_k^+, \tag{4}$$

where $\phi_k(r)$ and $a_k^+$ are the single-particle states and creation operators, respectively. In Eq. (2) the operator $M$ acts on $\rho_{0\lambda}(\mathbf{r}',\mathbf{r})$ before integration. In the EOM method[1] the transition density is defined by the amplitudes $Y_{m\nu}$ and $Z_{m\nu}$ through

$$\rho_{0\lambda}(\mathbf{r}',\mathbf{r}) = \langle 0|[\rho, O_\lambda^+]|0\rangle. \tag{5}$$

TABLE I. Transition moments between excited triplet states.[a]

| $R$(a.u.) | $R$(Å) | TDA | RPA | HRPA | TDA | RPA | HRPA |
|---|---|---|---|---|---|---|---|
| | | $B\,^3\Pi_g - W\,^3\Delta_u$ | | | $B\,^3\Pi_g - A\,^3\Sigma_u^+$ | | |
| 1.701 | 0.90 | 0.308 | 0.318 | 0.311 | 0.329 | 0.350 | 0.362 |
| 1.890 | 1.00 | 0.295 | 0.312 | 0.300 | 0.301 | 0.338 | 0.318 |
| 2.068 | 1.094[b] | 0.227 | c | 0.284 | 0.280 | c | 0.296 |
| 2.268 | 1.20 | 0.250 | c | 0.260 | 0.254 | c | 0.273 |
| 2.457 | 1.30 | 0.222 | c | 0.233 | 0.227 | c | 0.248 |
| 2.645 | 1.40 | 0.191 | c | 0.203 | 0.197 | c | 0.217 |
| | | $B\,^3\Pi_g - B'\,^3\Sigma_u^-$ | | | $B\,^3\Pi_g - C\,^3\Pi_u$ | | |
| | 0.90 | 0.308 | 0.306 | 0.308 | 1.53 | 1.55 | 1.55 |
| | 1.00 | 0.294 | 0.293 | 0.295 | 1.58 | 1.59 | 1.60 |
| | 1.094 | 0.274 | c | 0.277 | 1.59 | c | 1.62 |
| | 1.20 | 0.246 | c | 0.252 | 1.59 | c | 1.62 |
| | 1.30 | 0.215 | c | 0.224 | 1.57 | c | 1.61 |
| | 1.40 | 0.180 | c | 0.195 | 1.54 | c | 1.58 |

[a]Absolute value of the transition moment in atomic units. 1 a.u = 2.542 D. See text for discussion of the headings TDA, RPA, and HRPA.
[b]Experimental internuclear distance of the ground state.
[c]In this column we indicate an instability in this approximation.

  

TABLE II. Transition moments between excited singles states of $N_2$.[a]

| $R$(a.u.) | $R$(Å) | TDA | RPA | HRPA | TDA | RPA | HRPA |
|---|---|---|---|---|---|---|---|
| | | $a\,^1\Pi_g - w\,^1\Delta_u$ | | | $a\,^1\Pi_g - c'\,^1\Sigma_u^+$ | | |
| 1.701 | 0.90 | 0.269 | 0.269 | 0.266 | 0.729 | 0.701 | 0.951 |
| 1.890 | 1.00 | 0.263 | 0.263 | 0.263 | 0.430 | 0.404 | 0.555 |
| 2.068 | 1.094[b] | 0.245 | 0.246 | 0.248 | 0.295[c] | 0.195[c] | 0.385[c] |
| 2.268 | 1.20 | 0.218 | 0.220 | 0.224 | 0.251 | 0.252 | 0.334 |
| 2.457 | 1.30 | 0.188 | 0.194 | 0.196 | 0.179 | 0.166 | 0.269 |
| 2.645 | 1.40 | 0.155 | 0.176 | 0.167 | d | d | 0.233 |
| | | $a\,^1\Pi_g - b'\,^1\Sigma_u^+$ | | | $a\,^1\Pi_g - c'\,^1\Sigma_u^+$ | | |
| | 0.90 | d | d | d | 0.162 | 0.153 | 0.182 |
| | 1.00 | d | 0.043 | d | 0.044 | d | 0.138 |
| | 1.094 | 0.107[c] | 0.247[c] | 0.093[c] | d | d | d |
| | 1.20 | 0.051 | 0.066 | 0.027 | d | d | d |
| | 1.30 | 0.017 | 0.064 | 0.094 | d | d | d |
| | 1.40 | 0.0002 | 0.038 | 0.086 | d | d | d |
| | | $a\,^1\Pi_g - a'\,^1\Sigma_u^-$ | | | $a\,^1\Pi_g - b\,^1\Pi_u$ | | |
| | 0.90 | 0.307 | 0.311 | 0.312 | 1.45 | 1.47 | 1.42 |
| | 1.00 | 0.282 | 0.291 | 0.288 | 1.53 | 1.54 | 1.54 |
| | 1.094 | 0.256 | 0.271 | 0.263 | 1.54 | 1.56 | 1.57 |
| | 1.20 | 0.224 | 0.253 | 0.232 | 1.53 | 1.55 | 1.56 |
| | 1.30 | 0.191 | 0.264 | 0.200 | 1.51 | 1.54 | 1.54 |
| | 1.40 | 0.158 | e | 0.165 | 1.47 | 1.52 | 1.50 |

[a]Absolute value of the transition moment in atomic units (a.u.). 1 a.u. = 2.542 D. See text for discussion of the headings TDA, RPA, and HRPA.

[b]Experimental equilibrium internuclear distance of the ground state.

[c]The $b'\,^1\Sigma_u^+$ and $c'\,^1\Sigma_u^+$ states are close to each other at this geometry and there is significant mixing of the particle–hole amplitudes (one-electron excitations) usually associated with each state.

[d]At this geometry this $^1\Sigma_u^+$ states is not one of the two lowest $^1\Sigma_u^+$ states in this approximation.

[e]Unstable in this approximation.

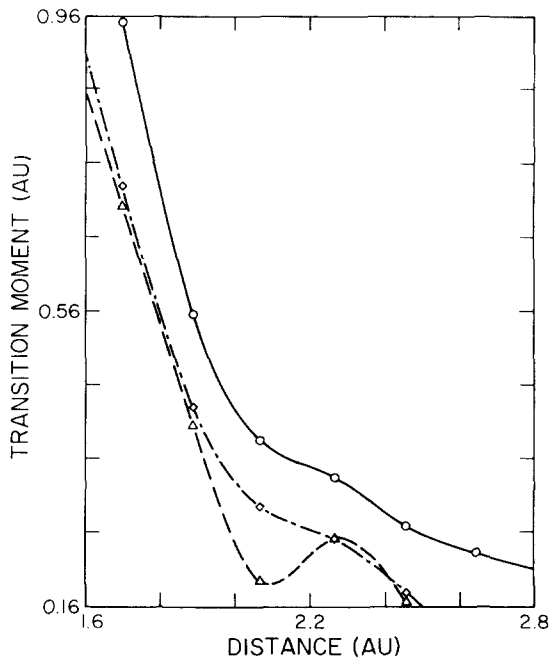


FIG. 2. Transition moment for the $a\,^1\Pi_g - c'\,^1\Sigma_u^+$ transition in the three different approximations. ——HRPA, – – – RPA, – ——— – TDA. See Ref. 3 and text for an explanation of these approximations.

In Eq. (5) $O_\lambda^+$ is the excitation operator defined such that $O_\lambda^+|0\rangle = |\lambda\rangle$.

If the operator $O_\lambda^+$ is restricted to single particle-hole form, i.e.,

$$O_\lambda^+ = \sum_{m\gamma} [Y_{m\gamma}(\lambda) a_m^+ a_\gamma - Z_{m\gamma}(\lambda) a_\gamma^+ a_m], \tag{6}$$

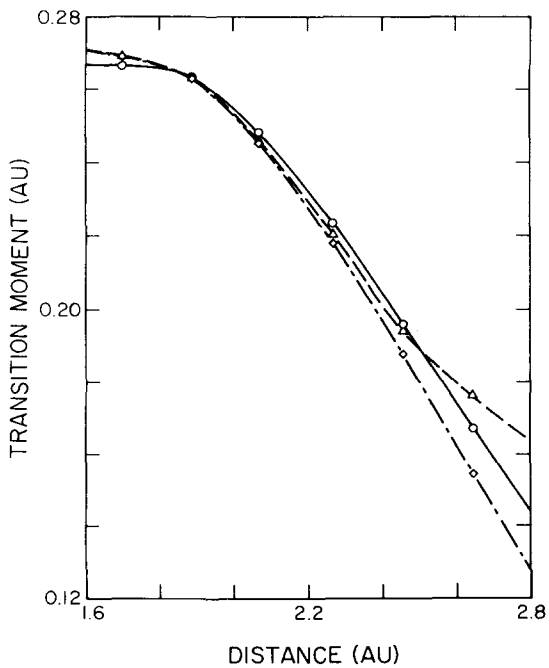


FIG. 1. Transition moment for the $a\,^1\Pi_g - w^1\Delta_u$ transition in the three different approximations. ——HRPA, – – – RPA, – ——— – TDA. See Ref. 3 and text for an explanation of these approximations.

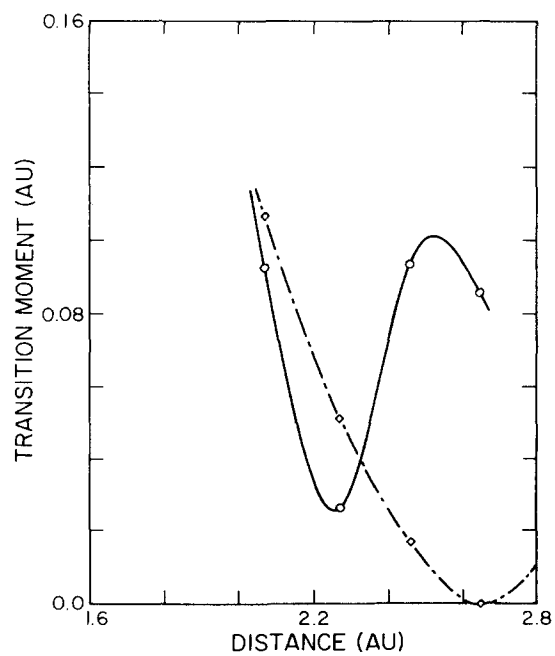


FIG. 3. Transition moment for the $a\,^1\Pi_g - b'\,^2\Sigma_u^+$ transition in the two different approximations. —— HRPA, – ——— – TDA. See Ref. 3 and text for an explanation of these approximations.

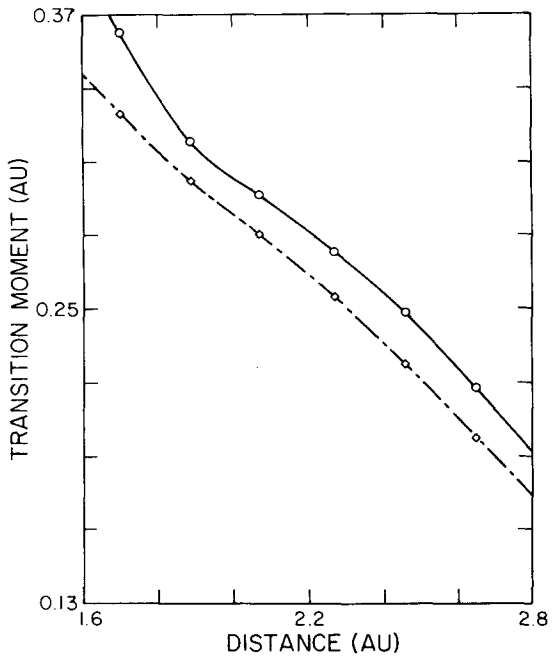


FIG. 4. Transition moment for the $B\,^3\Pi_g$–$A\,^3\Sigma_u^+$ transition in the two different approximations. —— HRPA, – ——– TDA. See Ref. 3 and text for an explanation of these approximations.

the amplitudes $Y_{m\gamma}(\lambda)$ and $Z_{m\gamma}(\lambda)$ satisfy the equation[3]

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} Y(\lambda) \\ Z(\lambda) \end{pmatrix} = \omega_{0\lambda} \begin{pmatrix} D & 0 \\ 0 & D \end{pmatrix} \begin{pmatrix} Y(\lambda) \\ Z(\lambda) \end{pmatrix}. \tag{7}$$

The equation of motion, Eq. (7), can be solved straightforwardly for the excitation energies $\omega_{0\lambda}$ and the amplitudes $Y(\lambda)$ and $Z(\lambda)$. The method has been shown to yield accurate dipole transition moments out of the ground state.

In Ref. 1 we showed how excited state–excited state transition moments could be obtained directly from the set of ground state–excited state transition densities $\{\rho_{0\lambda}\}$ derived from Eqs. (7) and (5). The details have been given previously[1] and here we will only discuss these results briefly. The basic procedure is to exploit the formal properties of the excitation operators $O_{\lambda i}^+$, $O_{\lambda i}^+|0\rangle = |\lambda_i\rangle$ and $O_{\lambda_i}|0\rangle = 0$, to rewrite the transition moment between the excited states $|\lambda_i\rangle$ and $|\lambda_j\rangle$, $\langle\lambda_i|M|\lambda_j\rangle$, as the expectation value of the commutators of the operators $O_{\lambda_i}$, $M$, and $O_{\lambda_j}^+$.

$$\langle\lambda_i|M|\lambda_j\rangle = \langle 0|[O_{\lambda_i}, M, O_{\lambda_j}^+]|0\rangle + \tfrac{1}{2}\langle 0|[O_{\lambda_i}, O_{\lambda_j}^+]M|0\rangle + \tfrac{1}{2}\langle 0|M[O_{\lambda_i}, O_{\lambda_j}^+]|0\rangle, \tag{8}$$

where the double commutator is defined as

$$2[A, B, C] = [[A, B, ], C] + [A, [B, C]]. \tag{9}$$

Equation (8) is an off-diagonal matrix element of the operator $M - \langle 0|M|0\rangle$. The diagonal elements of this operator, e.g., $\langle\lambda_i|M|\lambda_i\rangle - \langle 0|M|0\rangle$, are the changes in the expectation value of any operator upon electronic excitation. The latter will be discussed in a forthcoming paper.[4] The right-hand side of Eq. (8) is evaluated in three different approximations: the Tamm–Dancoff approximation (TDA), the random phase approximation (RPA), and higher random phase approximation (HRPA). These approximations have been discussed in detail previously.[1] The advantage in going from the expectation value of the direct product of the operators $O_{\lambda_i}$, $M$, and $O_{\lambda_j}^+$ to the expectation value of the double commutator of Eq. (8) is due to the observation that the double commutator is a simpler operator, and hence its expectation value is less sensitive to the details of the ground state wavefunction.[5]

We will use these three approximations to calculate the excited state–excited state transition moments. With little more effort than is involved in calculating excitation energies and ground state–excited state transition moments excited state–excited state transition moments can be determined by use of Eq. (8).

## III. RESULTS

The ground state electron configuration of $N_2$ is $(1\sigma_g)^2 \times (1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$. The principal electron configuration of the $A\,^3\Sigma_u^+$, $b'\,^1\Sigma_u^+$, $B'\,^3\Sigma_u^-$, $a'\,^1\Sigma_u^-$, $W\,^3\Delta_u$,

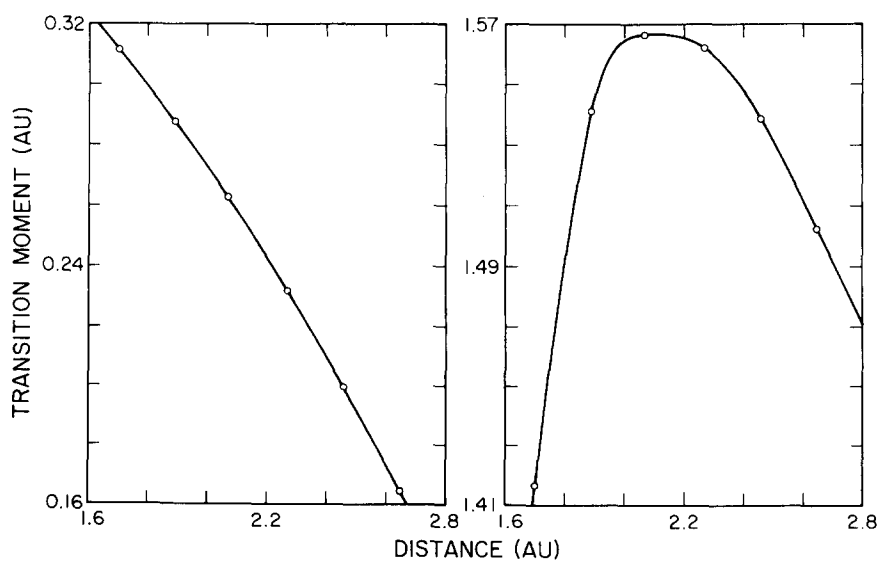


FIG. 5. HRPA transition moments for the $a\,^1\Pi_g$–$a'\,^1\Sigma_u^-$ transition (left) and the $a\,^1\Pi_g$–$b\,^1\Pi_u$ transition (right).

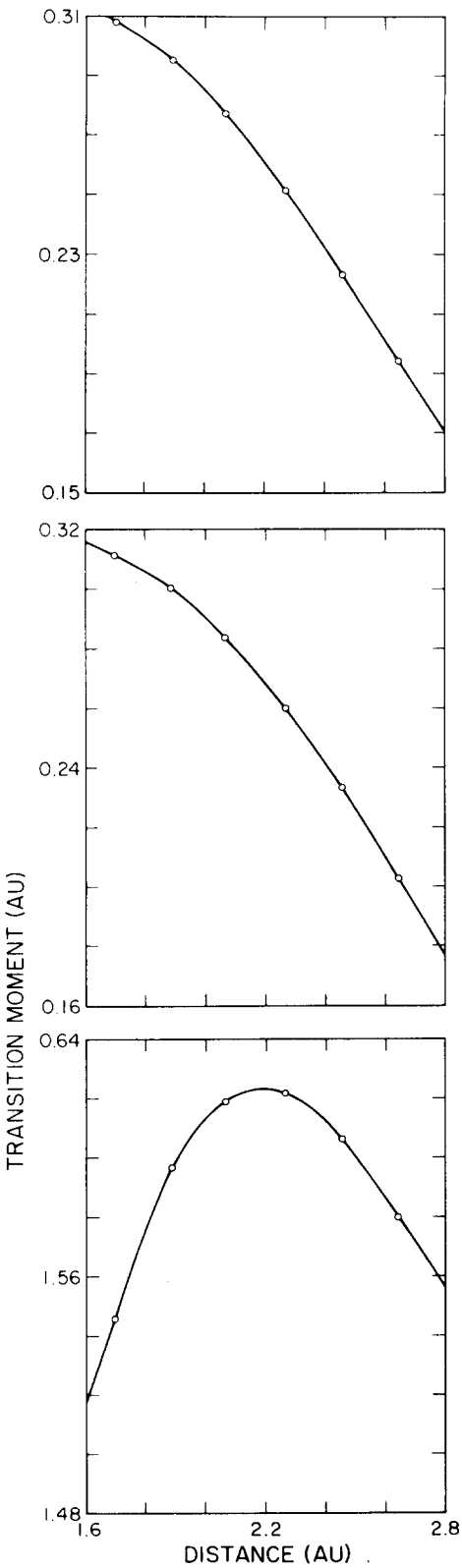


FIG. 6. HRPA transition moments for the $B\,^3\Pi_g$–$B'\,^3\Sigma_u^-$ transition (top), $B\,^3\Pi_g$–$W\,^3\Delta_u$ transition (middle), and the $B\,^3\Pi_g$–$C\,^3\Pi_u$ transition (bottom).

and $w\,^1\Delta_u$ states is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(1\pi_g)$ and that of $B\,^3\Pi_g$ and $a\,^1\Pi_g$ state is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2 \times(1\pi_u)^4(3\sigma_g)(1\pi_g)$. In a previous paper[6] we reported the excitation energies and dipole transition moments from the ground state to these excited states at several internuclear distances. The basis set consists of a valence $[4s3p]$ basis contracted from a $(9s5p)$ set of primitive Gaussian functions plus two diffuse $d\pi$ and $p\sigma$ functions at the center of the molecule. This basis set and other details are given in Ref. 6. We now use the transition densities and other results of these calculations to calculate the absolute value of the transition moments between the excited states of $N_2$.

Tables I and II give these transition moments for the triplet–triplet and singlet–singlet transitions, respectively. The results should be immediately useful in constructing the line strengths of these electronic transitions. For some transitions a linear approximation to the variation of the transition moment with $R$ is adequate over this range of internuclear distances. If adequate vibrational wavefunctions for these states are calculated, some interesting tests of the $R$-centroid approximation can be made.[7]

From Table I we see that the transition moments for the $B\,^3\Pi_g$–$W\,^3\Delta_u$ and $B\,^3\Pi_g$–$A\,^3\Sigma_u^+$ transitions are almost equal and both show considerable $R$-dependence. In their model calculations Cartwright *et al.*[8] assumed values for the $B \rightarrow W$ transition moment equal to 1.7 and 0.85 of the $B \rightarrow A$ transition moment at $R = 1.3$ Å since no calculated or experimental value was available. These choices were made to see the effect of this transition moment on the predictions of their models. We see that the assumptions of $M(B \rightarrow W) = 0.85\ M(B \rightarrow A)$ is in fact close to our predictions which show these two transition moments to be approximately equal.

We also comment on the transitions involving the $^1\Sigma_u^+$ states. Avoided crossings among these states make them interesting. The $c'$ state is primarily a $3\sigma_g \rightarrow 3\sigma_u$ excitation, the $b'$ state $\pi_u \rightarrow \pi_g$, and the $e'$ state $3\sigma_g \rightarrow 4p\sigma$. These are deperturbed states[6,9] which correspond to hypothetical electronic states of the same symmetry which are allowed to cross. For the $^1\Sigma_u^+$ states we have simply used the lowest two $\Sigma_u^+$ states in our calculations. Neither the $b'$ nor the $e'$ states is always one of the two lowest states, and the relative ordering may differ some what depending on the approximation used.

Figures 1–6 show the transition moments of several transitions in various approximations. In general the HRPA results should be regarded as the most reliable.

A detailed comparison with experimental results is somewhat difficult. In extracting the transition moment from an analysis of band intensities the variation of the transition moment is usually expressed in terms of the $R$-centroid variable.[10] The results in this paper along with reliable vibrational wavefunctions should be used in the analysis of the observed band intensities. In fact, the present results should simplify the analysis of such intensities. We do note that our calculated transition moment of 0.27 a.u. at $R = 1.2$ Å for the $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ transition agrees well with the value of about 0.31 a.u. determined from experimental intensities.[10,11]

## IV. CONCLUSIONS

We have used a recently proposed many-body theory—the equations of motion method—to calculate the transi-

tion moments between many of the excited states of $N_2$. These transition moments are obtained as a function of internuclear distances from 0.90 to 1.40 Å. Along with reliable vibrational wavefunctions these results can be very useful in the analysis of experimental intensities and, in fact, such results could be used to test the $R$-centroid approximation for a variety of transitions in $N_2$. It is encouraging that these transition moments between excited states can be obtained with only a slight increase in the effort needed to obtain the ground to excited state transition moments.

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