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# Molecular-Orbital Calculation of the Shape Resonance in $N_2^-$[†]

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The 2-eV shape resonance in $N_2$-electron scattering is calculated by a self-consistent-field energy-variational procedure. The resonance state corresponds to the attachment of an incident $d$-wave electron to the $1\pi_g$ valence orbital of the metastable $^2\Pi_g$ state of $N_2^-$. The resonant behavior is due to the tunnelling of the electron through a $2(2+1)/r^2$ centrifugal barrier and temporary trapping in an attractive field. This tunnelling is reflected in the bimodal behavior of the calculated $1\pi_g$ orbitals; the inner portion of the orbital defines the resonance state. The "potential" curve for $N_2^-$ is calculated in the Hartree-Fock approximation; a resonance threshold of 2.5 eV is predicted, with $R_e = 2.27$ a.u. and $\omega_e \approx 2000\ \text{cm}^{-1}$. Expected correlation-energy corrections would improve the agreement with experiment. A local potential for electron scattering is generated by inverting the $1\pi_g$ orbital, and resonance widths are calculated. The widths vary from 0.13 eV at the equilibrium distance of $N_2^-$ to 0.8 eV at the $N_2$ equilibrium distance.

## I. INTRODUCTION

The resonance structure in electron scattering from $N_2$ is due to "attachment" of the $d$ wave of the incident electron to the first unoccupied $\pi_g$ valence orbital. In terms of a "local" potential, the incident electron penetrates or tunnels through a barrier that can be represented asymptotically as

$$V_{r\to\infty} \sim -\alpha_0/2r^4 + 2(2+1)/r^2 \ . \qquad (1)$$

At short range, of the order of the size of the molecule ($\sim 1.5$ a.u.), the potential is attractive and, for $E \sim 2$ eV, sufficient to support a metastable "bound" state. This picture was developed by Bardsley, Mandl, and Wood.[1] A $^2\Pi_g$ configuration for the $N_2^-$ had been proposed earlier by Gilmore[2] on the basis of molecular-orbital theory and an estimate of a real $N_2^-$ potential energy curve was made. Chen[3] has deduced a similar curve semi-empirically and the angular dependence of the scattered electron[4] is consistent with the $^2\Pi_g$ resonant state of $N_2^-$. Although the qualitative structure of the resonance state now appears to be understood, *a priori* calculations based on the molecule itself are lacking.

In this paper, we calculate the resonance state of $N_2^-$ from molecular-orbital theory and use this to develop a local potential for electron scattering. The scattering wave function is assumed to be expanded in terms of a tight resonance state with decaying boundary conditions and appropriate phase-shifted continuum functions. Since we are concerned only about resonant scattering, where the electron penetrates into a well of the size of the molecule, we assume that a knowledge of the resonance function alone can be used to determine the "local" potential that supports the resonance state. This potential includes both exchange effects and the electrostatic polarization of the target molecule but does not include correlation. The long-range part of the potential is approximated by the centrifugal term plus the isotropic part of the asymptotic adiabatic-polarization potential[5] in Eq. (1). This is joined to a potential that is obtained by inverting the Schrödinger equation for the resonance state function. The one-electron potential is then used to estimate the scattering phase shift and the resonance width.

## II. RESONANCE STATE AND APPROXIMATE POTENTIAL ENERGY CURVE OF $N_2^-$

The resonance state function is approximated by a self-consistent field (SCF) wave function of $N_2^-$ that is calculated with an expansion trial function composed of Gaussian-type functions (GTF) centered at both of the atom centers and the center of the molecule.[6] The ground state of $N_2^-$ is represented by the configuration

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g,\ {}^2\Pi_g\ .$$

Since the SCF function for $N_2$ for any trial function set has a lower energy, it is possible by varying the exponents of the GTF in the $N_2^-$ wave function to obtain a wave function that describes the neutral $N_2$ molecule and a zero-energy continuum electron (whose wave function is a constant).[7] However, if the exponents of the GTF for the $1\pi_g$ orbital are chosen so that the Gaussian half-widths are less than 6 a.u., it is found that the SCF variation of the linear coefficients does not yield a continuumlike orbital. In fact, the $1\pi_g$ orbital is barely distinguishable from a $1\pi_g$ orbital calculated for any valence excited state of $N_2$, e.g.,

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g 1\pi_g,\ {}^{1,3}\Pi_g\ .$$

The orbital senses the centrifugal barrier. This is demonstrated in Fig. 1(a) where the $N_2^-$ $1\pi_g$ orbital is compared to that of the ${}^1\Pi_g$ state of $N_2$. When the GTF are chosen with sufficiently large exponents, they decay before the long-range repulsive potential has dropped below the positive orbital energy of the $1\pi_g$. In the spatial region of the ground state $N_2$, the $1\pi_g$ orbital agrees with the excited valence orbital and decays as it encounters the repulsive barrier. Varying the exponents on the *d* functions at the molecule center permits the charge density to accumulate at large distances beyond the repulsive barrier. For GTF with half-widths to 10 a.u., the $1\pi_g$ orbital becomes bimodal as shown in Fig. 1[8]; however the curvature of the inner maximum remains the same and produces an almost identical "local potential" as shown in Fig. 1(b). This is discussed more fully in Sec. III.

The requirement that a low-energy valence orbital is available may be an important restriction on the formation of resonance states. Valence orbitals are the size of the ground state of the molecules and the electron can be trapped within the barrier because a large, attractive potential is available. Rydberg-type orbitals on the other hand are characterized by a large radius well outside the initial ground-state distributions. There are only a very few valence-type orbitals normally available; excitation is primarily to Rydberg-type states. In $N_2$, for example, it is normally presumed that there is one other valence-type orbital that is available, the $3\sigma_u$, which could support a *p*-type resonance. However, a calcula-

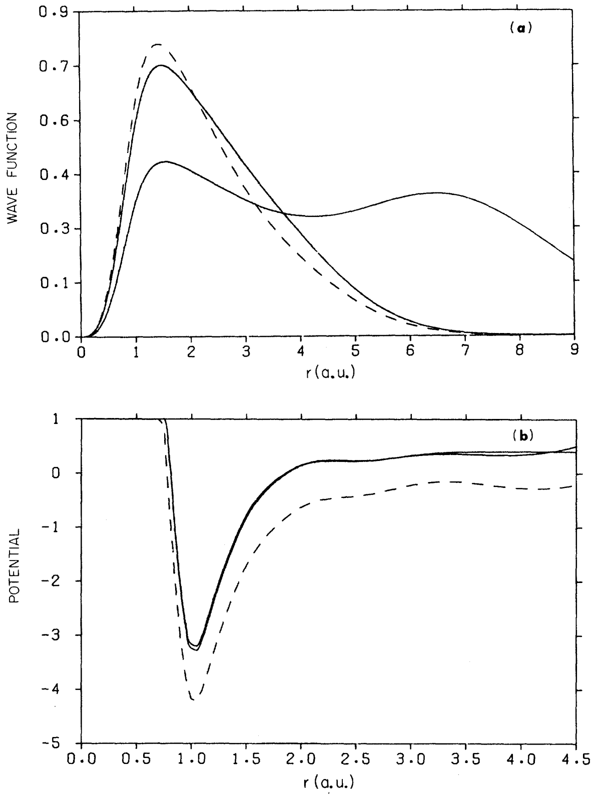

FIG. 1. (a) Plot of the $l = 2$ Legendre component of the $\pi_g$ orbital wave functions. The dashed curve is from the ${}^1\Pi_g$ excited valence state of $N_2$. The solid curves are the $N_2^-$ orbitals; both the constrained orbital which does not contain any *d* functions, and the more extended, bimodal function which has three *d* functions which permit the orbital to "tunnel" through the centrifugal barrier exhibit a large amplitude peak at $r \approx 1.2$ which is similar to the ${}^1\Pi_g$ orbital. The shape resonance state is "defined" by this inner portion of the $\pi_g$ orbital of $N_2^-$. (b) The "local" potentials which are generated by the three $\pi_g$ orbitals in Fig. 1(a) are seen to be very similar. Since the ${}^1\Pi_g$ orbital is truly bound, the well is slightly deeper. In spite of the marked redistribution of the charge in the $N_2^-$ orbitals, their potentials are quite similar for $r < 2.2$; the invariability of the local potential is used as a criterion for defining the shape resonance state.

tion of the configuration

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g 3\sigma_u, \ {}^1\Sigma_u^+$$

yields a $3\sigma_u$ orbital that is primarily Rydberg. The variational determination of the $3\sigma_u$ orbital prefers to find the charge density of a $3p$ function rather than a tight valence-type density. This indicates that a local potential is not sufficiently deep to support such a valence state and no resonance should be expected from attachment to the $3\sigma_u$ orbital. It is important that the valence or Rydberg character of available orbitals be determined. *Only the valence-type functions will support a shape resonance.*

The decreased amplitude of the $1\pi_g$ in the vicinity of 4 a.u. is indicative of the presence of the barrier. The resonance state is defined essentially for $r$ less than 4 a. u. A sufficiently large basis is used to provide an adequate description of the wavefunction in the neighborhood of the barrier. However, the wave function is not obtained to very high accuracy on the periphery of the molecule due to the energy weighting inherent in an SCF calculation. This is in addition to the inaccurate asymptotic dependence of the GTF which manifests itself beyond 5 a. u. for the basis used. The accuracy of the function in the neighborhood of the first maxima was gauged by the invariability of the local potential obtained with different size trial functions. The results are all based on "double $\zeta$" quality GTF[9] for the core functions and up to a 4GTF set of $d$-type functions centered at the c. m.

The energy curve for a GTF set that deletes the $d$-type orbitals and retains only $p\pi_A - p\pi_B$, $\pi_g$-type functions is given in Fig. 2. As long as the $\pi_g$ electron is within the barrier, the variation of total energy with and without the $d$-type functions is only of the order of the anticipated width, i. e., 0. 1 eV. Although these curves can be in serious

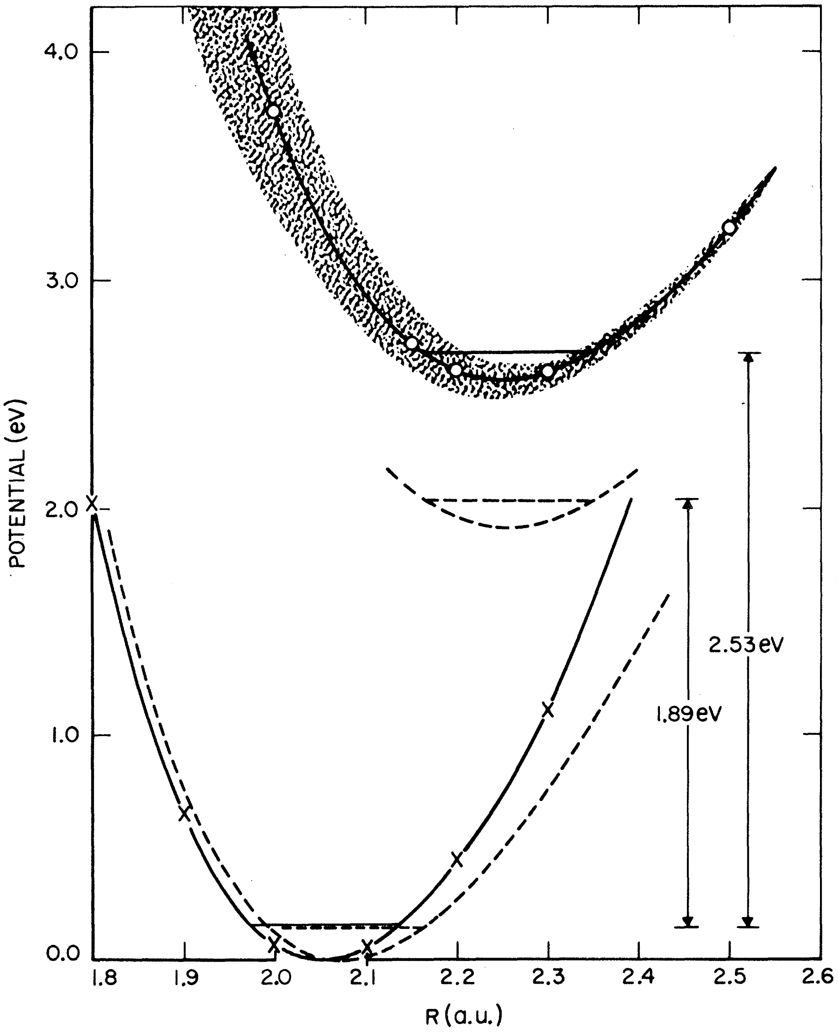

FIG. 2. Potential curves for $N_2$ and $N_2^-$. The solid curves are the calculated HF potentials and predict a resonance energy of 2. 53 eV for the $v=0$ state of $N_2^-$. The dashed curves are the experimentally observed potentials. A correlation-energy correction of 0. 67 eV with respect to $N_2$ has been applied to the $N_2^-$ curve to bring the $v=0$ level in coincidence with the observed resonance at 1. 89 eV. This correction is strictly valid at the $N_2^-$ equilibrium distance $R \approx 2.27$ and we can not have much confidence in the shape of the curve at distances far from equilibrium. The $N_2^-$ curve is shaded to indicate this in a *metastable* state and must be defined by a complex "potential" which includes a width for auto-ionization. The shaded area approximates our calculation of the resonance widths.

error due to correlation errors as well as the failure to obtain the Hartree-Fock (HF) limit, the calculated HF resonance energy, ≈ 2.53 eV, is remarkably close to the experimental value of 1.89 eV. The correlation energy problem is complicated by the asymptotic error in a HF calculation of $N_2$ or $N_2^-$ ground states as the internuclear distance goes to infinity. This will be less severe in $N_2^-$ than $N_2$ and appears to offset the additional correlation energy expected from adding a penetrating electron to $N_2$. On comparison with experiment the additional correlation energy obtained by adding one electron to the ground state is 0.67 eV. An estimate of these corrections can be made by comparison of the HF calculations to the experimental values in $O_2 - O_2^-$. These estimates[10] predict a relative lowering of the $O_2^-$ curve by about 0.8 eV and are consistent with the $N_2$-$N_2^-$ observations. Only a correlation-energy calculation can properly answer what the correction should be.

One feature of these energy curves of interest is the equilibrium internuclear distance. The metastable $N_2^-$ curve is not clearly defined but, if the real parts of the inherently complex nuclear potential behave like the $N_2$ curve, it is expected that the $R_e$ is to the right of the present calculated value by about 0.02 a.u. or $R_e$ is 2.27 a.u. This would imply that the $N_2$ and $N_2^-$ curves do not cross until much larger $R$.[11] The predicted HF spectroscopic constants for $N_2^-$ are $\omega_e \approx 1960\ \mathrm{cm}^{-1}$, $\omega_e x_e = 9\ \mathrm{cm}^{-1}$; however there is usually a considerable correlation correction to the spectroscopic constants.

## III. DETERMINATION OF LOCAL POTENTIAL FOR ELECTRON SCATTERING BY $N_2$

The molecular-orbital function $1\pi_g$ which is obtained in the SCF calculations is expanded in spherical harmonics

$$\psi_{\pi_g} = \Sigma_l Y_{l,1}(\theta, \varphi)[\rho_l(r)/r] \tag{2}$$

about the molecule center. The function is used to obtain a scattering potential by solving the equation

$$(\tfrac{1}{2}\nabla^2 + E_0 - V)\psi_{\pi_g} = 0, \tag{3}$$

to obtain a "local" potential $V$ which reproduces the orbital in the regions $r < r_{\max}$, where $E_0$ is the energy difference between the $N_2$ and $N_2^-$ states. This potential differs from the usual polarization potential[12] since $\psi_{\pi_g}$ describes an electron distribution and not a point electron but it includes both exchange and all the proper electrostatic interactions, including the relaxation of the $N_2$ core in an SCF manner.

To a first approximation we neglect coupling to higher partial waves and take

$$\psi_{\pi_g} \approx Y_{2,1}(\theta, \varphi)[\rho_2(r)/r] , \tag{4}$$

and determine the radial potential

$$V_2(r) = U(r) + 2(2+1)/r^2 .$$

The "local" potentials are determined for three $N_2^-$ internuclear distances,[13] $R = 2.0$, 2.15, and 2.3 a.u. The largest GTF set that retained the electron density within the barrier is identified with the resonance state. An arbitrary criterion is used, i.e., the amplitude of the $\pi_g$ orbital at the first maximum $r \approx 1.2$ should not decrease by more than 10% compared to the orbital without any $d$ functions, in which case the energy of $N_2^-$ decreases by not more than 0.1–0.2 eV. The most extended basis set can be used for $R = 2.3$, while the most contracted is required for $R = 2.0$, suggesting that the degree of tunnelling, and hence the width, increases markedly with decreasing $R$.

As in Fig. 1(b) all the calculated $\pi_g$ orbitals yield an attractive potential of about 3 a.u. in the vicinity of $r = 1.2$ a.u., pass through zero at $r \approx 2.0$ a.u., and mount to a repulsive "centrifugal" barrier at about $r = 3.0$–$3.5$ a.u. For $r < 2.2$ a.u., the potential is invariant to wide variations in the basis sets. Even when 75% of the charge is outside the barrier, as in the bimodal function in Fig. 1 (a), only minor changes occur. This is indicated by the orbitals of the target molecule which undergo only minor changes as the tight part of the $\pi_g$ orbital is gradually filled with increasing charge; this is a reflection of the low polarizability of $N_2$.[8]

Unfortunately, these potentials are not well represented beyond $r = 2.2$, and the shape and height of the barrier are very dependent on the basic set. A typical barrier is shown by the solid curve in Fig. 3, which is obtained with four $d$ functions for $R = 2.3$. Varying the number of $d$ functions causes the height to vary in the range from 4 to 5.5 eV. The $d$ functions were chosen to span this region, but the energy obtained in the SCF calculation is insensitive to the shape of the orbital in the region of the barrier.

Fortunately, the magnitude of the widths is dominated by the tunnelling through the long-range polarization potential. Two approximations were made, as indicated by the dashed curves in Fig. 3. The calculated local potential was employed up to either case (I) $r \approx 2.1$, or case (II) just past the maximum at $r \approx 3.5$, and the asymptotic form (1), chosen with an appropriate polarizability to match $V(r)$, was used for larger $r$.[14] The widths calculated with both potentials agree to within 10–20% (see Figs. 4 and 5) which is well within the range of other uncertainties.

Because of this difficulty in generating a proper

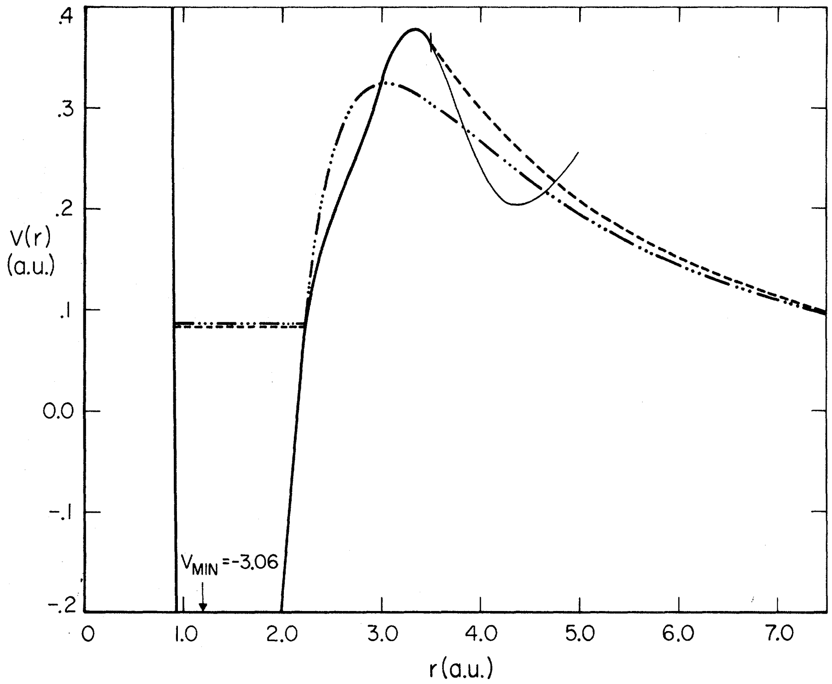

FIG. 3. Local potential for N$_2^-$ (2.3) in the vicinity of the barrier. The solid curve is the potential calculated from the $\pi_g$ orbital using a basis set containing five $p$ functions at each atom and four $d$ functions at the center. The height of the barrier varies by 0.07 a.u. depending on the number of $d$ functions used, and the shape, particularly to the right of the barrier, is variable and meaningless. However the potential to the left of $r = 2.2$ is invariant to the basis set. Two approximations were made for calculation of the tunnelling widths. Case I, the asymptotic polarization potential was fitted to the $V(r)$ potential at $r = 2.2$, with an $\alpha \approx 3.5$ Å$^3$, and case II, a fit was made at the barrier, $r = 3.5$ with $\alpha \approx 1.7$ Å$^3$. The position of the resonance is shown; case I predicts a width of 0.12 eV, and case II, a width of 0.10 eV.

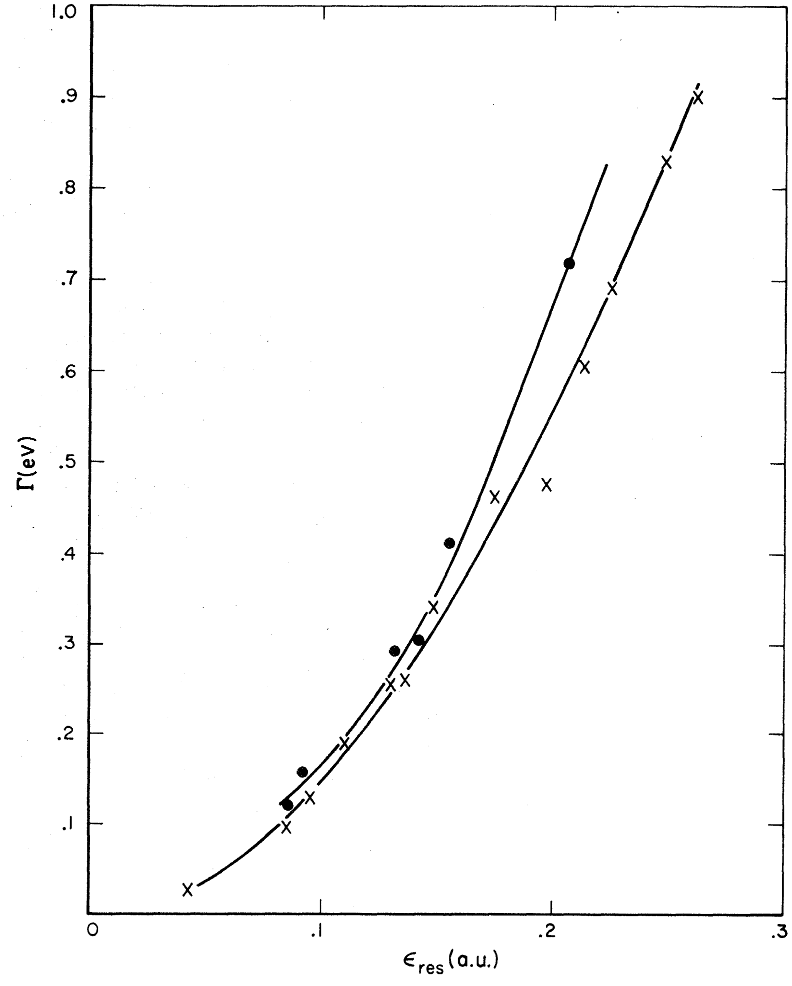

FIG. 4. Plot of calculated widths Γ versus resonance energy $\epsilon_{res}$ for a large variety of case-I (points) and case-II (crosses) potentials. Included on the graph are widths for three $R$ values, different values of $E_0$, and basis sets with variable number of $d$ functions. The curves are drawn through the two sets of points to demonstrate the range of widths that are obtained with these rather diverse centrifugal barriers (see Fig. 3). The agreement is quite good and demonstrates that it is the long-range tunnelling through the barrier which dominates the width calculations. The important feature to note is the marked sensitivity of the width to the resonance energy, and hence to the value of $E_0$ which is employed in the radical equation (3).

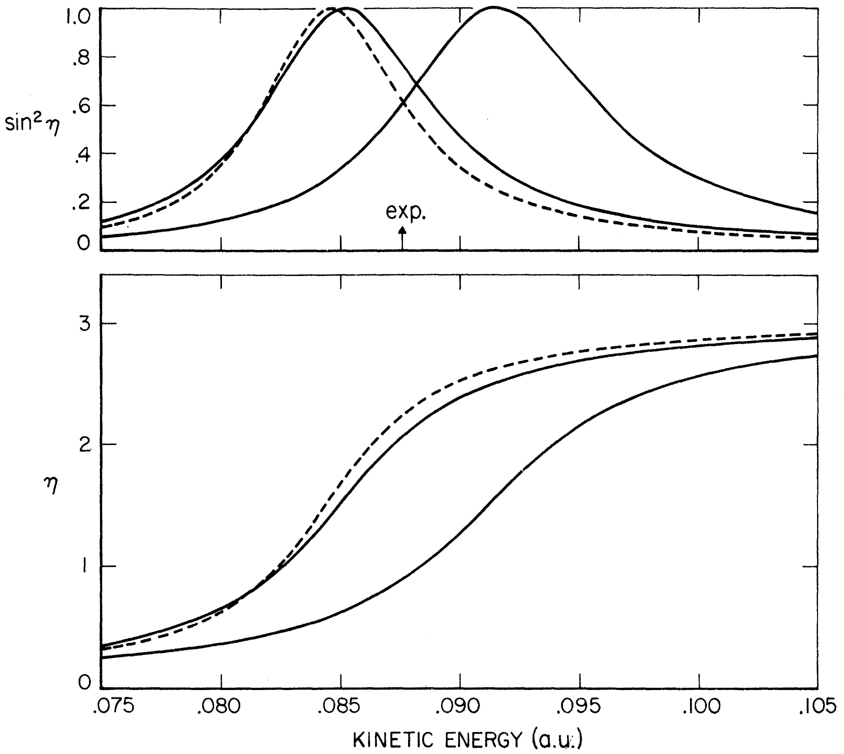

FIG. 5. Plot of phase shift $\eta(\epsilon)$ and $\sin^2\eta$ versus incident kinetic energy $\epsilon$ calculated for the potentials in Fig. 3. The solid curves are for case I using two different values of $E_0$. The experimental value of the resonance energy is intermediate (see arrow in upper plot) between the calculated resonance positions and the width, which is 0.12 and 0.155 eV for the two calculations, is predicted to be about 0.13 eV at the exact position. The dashed curve is the corresponding calculation using the case-II potential and predicts a width of 0.10 eV at the lower energy and 0.13 eV (not shown) at the higher $E_0$. Greater confidence is given to the case-I potential, and the width at $R=2.3$ is estimated to be $0.13\pm0.03$ eV.

local potential in the region between $r\approx 2.2$ where the resonance function is valid, and some unknown distance where the asymptotic potential is valid, we are convinced that the ultimate use of the resonance wave function should be as a basis function in a full variational scattering calculation,[15] or in a configuration-interaction calculation along the lines taken by Altick[16] for atoms. However, until such time as correlation effects can be incorporated into the wave function it is felt that the present approach is more accurate, since adjustments can be made for the neglected correlation energy which significantly affects the calculated width.

## IV. CALCULATION OF RESONANCE WIDTHS

It is straightforward to integrate the radial equation (3) and obtain the phase shift $\eta(\epsilon)$ for a $d$-wave electron in these local potentials.[17] There is a rapid variation of $\eta$ with incident kinetic energy $\epsilon$ in the vicinity of the "resonance energy" $\epsilon_{\mathrm{res}}\approx E_0$, and the slope can be used to define a resonance width $\Gamma$:

$$\eta(\epsilon_{\mathrm{res}})=\tfrac{1}{2}\pi,\ 2\frac{d\epsilon}{d\eta}\bigg|_{\epsilon=\epsilon_{\mathrm{res}}}\approx\Gamma\ .$$

For potential scattering, where the well cannot support a true bound state, the phase shift is zero at $\epsilon=0$, and may come close to, but never reach $\pi$ in the vicinity of the shape resonance, and then gradually tails off to zero at very large energies.[18] This shape resonance behavior is seen in Fig. 4, which shows the phase shifts and cross sections calculated for the potentials plotted in Fig. 3. It is somewhat different from the usual Fano or Feshbach closed-channel resonance, which is a many-body effect, where the phase shift must increase by $\pi$, and (as it passes through $\pi$) yield a zero cross section (a Fano-Beutler shape) in the vicinity of the resonance for a single open channel.

The calculated widths are critically dependent on the "resonance energy" $E_0$,[19] since this determines the thickness of the barrier through which the wave function must penetrate, and it is for this reason that correlation-energy corrections can play a critical role in determining the width. This is indicated in Fig. 5 where the calculated width is plotted *vs* $\epsilon_{\mathrm{res}}\approx E_0$ for a large variety of basis sets and $R$ values, and for different choices of $E_0$. The circles correspond to case-I potentials [matching Eq. (1) to $V(r)$ at $r\approx 2.0$] and the crosses to case-II potentials [matching Eq. (1) to $V(r)$ at the barrier]. Note the rapid increase in $\Gamma$ with increasing resonance energy. The correlation correction can change $E_0$ by 0.05 a.u. and lead to a factor of 2 change in the predicted width.

As shown by the dashed curves in Fig. 2, a correlation correction of 0.67 eV must be applied to our calculated values of $E_0 = E_{\mathrm{HF}}(\mathrm{N}_2^-) - E_{\mathrm{NF}}(\mathrm{N}_2)$ to bring the position of the $\mathrm{N}_2^-$, $v=0$ vibrational level into agreement with experiments. The widths, calculated with these corrected energies, are those given in Table I. The estimated errors are somewhat arbitrary, and are as likely imposed by uncertainties in the proper resonance energies as any subtleties in the shape of the barrier. Greatest confidence is given to case-I calculations, and case-II widths are used primarily to judge the sensitivity of the widths to changes in the potential barrier.

## V. CONCLUSIONS

The conclusions of this study can be summarized as follows:

(a) The molecular-orbital description of a shape resonance exhibits the qualitative features predicted by Bardsley *et al.*[1] of tunnelling through a centrifugal barrier and attachment to a penetrating valence-type low-energy orbital.

(b) Resonance energies which are obtained are in quantitative agreement with observations if proper account is taken of correlation-energy corrections to the HF energies.

(c) The potential-energy curve calculated for $\mathrm{N}_2^-$ predicts a shift of 0.20 a.u. in $R_e$ from $\mathrm{N}_2$ to $\mathrm{N}_2^-$ and a $\omega_e = 1960\ \mathrm{cm}^{-1}$ for $\mathrm{N}_2^-$.

TABLE I. Resonance widths and energies.

| $R$ (a.u.) | Width (eV) | $E_{\mathrm{res}} = \epsilon_{\mathrm{res}} + [V_{\mathrm{N}_2}(R) - V_{\mathrm{N}_2}(R_{eq})]$ |
|---|---|---|
| 2.3 | 0.13 ± 0.03 | 1.947 eV |
| 2.15 | 0.29 ± 0.06 | 2.07 |
| 2.0 | 0.8 ± 0.3 | 3.07 |

(d) Inversion of the penetrating orbital to obtain a local potential yields an invariant and probably valid potential throughout the attractive region. This potential properly includes exchange and polarization effects. However, it is difficult to make a proper connection to the asymptotic polarization potential, and a crude joining was made either in the region of the centrifugal barrier, or at $V(r) \approx 0$.

(e) The width of shape resonances will be very sensitive to correlation effects because of the critical role played by the exact location of the resonance energy in determining the extent of tunnelling. If the energy is scaled to the experimental value the calculated width is of the order of 0.13 eV at $\mathrm{N}_2^-(R_e)$.

(f) The resonance width is a rapidly varying function of $R$ for $\mathrm{N}_2$, and increases from 0.13 at $R = 2.3$ to 0.8 eV at $R = 2.0$.

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[4] H. Ehrhardt, L. Langhaus, F. Linder, and H. S. Taylor, Phys. Rev. 173, 222 (1968).

[5] In the case of $\mathrm{H}_2$, this is a good approximation for $r$ greater than three times the internuclear distance. See N. E. Lane and R. J. W. Henry, Phys. Rev. 173, 183 (1968).

[6] The SCF calculations were performed on a modified version of IBMOL-2 written by E. Elementi and D. R. Davis of IBM Research Laboratory. See, J. Comput. Phys. 1, 223 (1966).

[7] A similar situation has been examined for $\mathrm{H}_2$: E. R. Davidson, J. Chem. Phys. 36, 1080 (1962); H. S. Taylor and F. E. Harris, *ibid.* 39, 1012 (1963).

[8] Similar bimodal behavior was obtained in a $\mathrm{Ca}^-\,3d$ orbital supplied by A. W. Weiss, which suggests that a broad-shape resonance might exist at about k.e. ≈ 3 eV. However, due to the extreme polarizability of the Ca core, the "local" potential generated for the $d$-wave electron varies radically with the amount of penetrating charge in the $d$ orbital.

[9] See E. Clementi, J. Chem. Phys. 40, 1944 (1964).

[10] An estimate has been made of the additional correlation energy upon the addition of one electron to $\mathrm{O}_2(^3\Sigma_g^-)$ resulting in the $^2\Pi_g$ ion ground state using bases comparable to those used for $\mathrm{N}_2$. The additional correlation energy in $\mathrm{O}_2$ is about 0.8 eV for this Gaussian calculation.

[11] A recent analysis of the scattering by A. Herzenberg [J. Phys. B 1, 548 (1968)] determines that the shift in $r_e$ from $\mathrm{N}_2$ to $\mathrm{N}_2^-$ is about 0.3 a.u. which is 0.1 a.u. larger than calculated here.

[12] See references cited in Ref. 5.

[13] The internuclear distance is represented by $R$, while $r$ refers to the electron coordinate for some fixed $R$ value.

[14] Polarizabilities are in the range 1.7 – 3.6 Å$^3$; the larger value for case I; the smaller for case II.

[15] See for example, R. K. Nesbet, Phys. Rev. 179, 60 (1969), and references cited therein.

[16] P. Altick, Phys. Rev. 169, 21 (1968).

[17] The algorithm developed by R. Gordon [J. Chem. Phys. 51, 14 (1969)] was employed.

[18] See discussion of Levinson's theorem, e.g., N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford U.P., London, 1965), 3rd ed., p. 156.

[19] Depending on the shape of the barrier, there is a shift in the position of the calculated resonance energy with respect to the approximate $E_0$ value. For example, in Fig. (5) a value of $E_0 = 0.0876$ was used for one of the calculations, with a resultant resonance energy $\epsilon_{\mathrm{res}}$ of 0.0852 for case I and 0.0846 for case II.