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Low-energy electron scattering by the NO molecule

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Abstract. Eigenphase sums and resonance positions and widths are calculated for low-energy elastic impact of electrons on NO molecules using the *R*-matrix method with numerically defined continuum orbitals. Calculations are performed using both the simple close-coupling and the close-coupling plus short-range polarisation models using up to six electronic states or pseudostates of the NO target. The open-shell, $^2\Pi$, target is found to show increased sensitivity to polarisation effects which are better represented by coupled-states calculations than by a one-state model with an optical potential. Comparison is made with the available experimental data on e-NO scattering.

1. Introduction

Recently there have been a number of calculations of phaseshifts and cross sections for the elastic scattering of low-energy electrons by diatomic molecules using the *R*-matrix formalism developed by Burke *et al* (1977). In particular, the adoption of numerically defined continuum basis functions (Burke *et al* 1983) has allowed the method to be applied to the impact of electrons on a variety of diatomics including N_2 (Burke *et al* 1983), F_2 (Morgan and Noble 1984) and the polar molecules CO and LiH (Salvini *et al* 1984). The method has also been extended to treat electronic excitation processes by the inclusion of several target eigenstates in the close-coupling expansion. Calculations include those on H_2^+ (Tennyson *et al* 1984, Tennyson and Noble 1985), H_2 (Baluja *et al* 1985) and O_2 (Noble and Burke 1986).

In these studies, polarisation effects were treated from first principles by a method that does not involve the introduction of any arbitrary parameters. Inelastic effects, which are not included explicitly in the close-coupling expansion, are included approximately via an optical potential (Burke and Noble 1983). Comparison with alternative methods of performing such calculations, including the linear algebraic approach (Schneider and Collins 1982) and the Schwinger multichannel variational method (Takatsuka and McKoy 1981), may be found in the reviews of Buckley *et al* (1984) and Burke and Noble (1986). In a recent collaborative study on electronic excitation of H_2, these methods gave results in good agreement with ours (Baluja *et al* 1985, Schneider and Collins 1985, Lima *et al* 1985).

NO is an interesting molecule because of the degeneracy of its X $^2\Pi$ ground state. While several experimental studies of e-NO scattering have been reported (Burrow 1974, Zecca *et al* 1974, Tronc *et al* 1975, Sanche and Schulz 1971, Ziesel and Field 1985), little theoretical work has been performed. Indeed the degeneracy of the NO ground state results in a lack of uniqueness for the symmetry of the scattering electron:

for example, it couples to both the σ and δ continua to give $^1\Pi$ and $^3\Pi$ scattering symmetries. This situation, as far as we are aware, has not previously been considered in *ab initio* molecular scattering calculations, although degenerate excited states have been used as part of a close-coupled expansion (e.g. Collins and Schneider 1983). Of course, the complications associated with spatial degeneracy will arise in many important cases, such as the photoionisation of O_2 (Roche *et al* 1981) and N_2 (Lucchese *et al* 1982). An analogous situation for atomic systems arises in the scattering of electrons by $2p^q$ open-shell atoms. These calculations have been performed for 20 years (Temkin 1957, Smith *et al* 1966).

An additional feature often associated with open-shell molecules is the presence of low-lying electronically excited states. These states have significant polarisation effects for elastic scattering even at energies where channels coupling to these states are closed. Although in principle one can include these effects via an optical potential, experience with H_2^+ (Schneider and Collins 1983, Tennyson *et al* 1984, Tennyson and Noble 1985) has shown convergence, at least for charged systems, to be slow. Electron collision calculations using many coupled states are now performed routinely for atomic targets (Berrington and Taylor 1982), but for molecular systems are still rare (see McKoy and Lee 1984).

Low-energy electron impact experiments (Burrow 1974, Zecca *et al* 1974, Tronc *et al* 1975) have yielded elastic and vibrational excitation cross sections which are characterised by strong energy-dependent structure resulting from resonant processes. These are associated with the presence of low-lying states of the NO^- ion. NO^- is isoelectronic with O_2 and the low-lying states are expected to be, by analogy, $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$. Although the existence of these states is well established, there is some disagreement between experimental results concerning their position and relative importance (lifetime). We expect that R-matrix calculations should resolve such questions since calculations on e–F_2 (Morgan and Noble 1984) have shown that the method gives the relative energies of F_2 and its negative ion with reasonable accuracy, something previous *ab initio* approaches only achieved by adjusting the F and F^- asymptotes. Moreover, since the anion energies are determined from R-matrix pole positions, direct information on the potential is available when the anion is both bound and unbound with respect to the neutral molecule.

In this work, we investigate low-energy e–NO collisions in both the resonant $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ and non-resonant $^1\Pi$ and $^3\Pi$ symmetries. This is done, first, in a one-state approximation, which allows us to investigate the channel coupling effects of the degenerate target; and, secondly, using up to six (nine if spatially degenerate states are counted twice) coupled states. These calculations represent the largest electron-molecule scattering calculations of this type yet reported, both in terms of number of coupled states and external channels (up to 40) explicitly included.

2. Theory

In the R-matrix method, the wavefunction of the scattering system is expanded within a finite spherical region of configuration space in the form

$$\Psi(x_1, x_2, \ldots, x_{N+1}) = \mathscr{A} \sum_{ij} c_{ij} \Phi_i(x_1, x_2, \ldots, x_N) F_{ij}(x_{N+1}) + \sum_j c_j \phi_j(x_1, x_2, \ldots, x_N, x_{N+1}) \qquad (1)$$

where x_i denote the space-spin coordinates of the N-electron target, x_{N+1} denotes the coordinates of the scattered electron and $\mathscr{A}$ antisymmetrises the coordinates of the target and scattered electrons. The Φ_i represent the target states explicitly included in the close-coupling expansion and the F_{ij} are continuum orbitals representing wavefunctions of the scattered electron.

In this work we used continuum functions centred at the NO centre of mass and defined as a product of spherical harmonics and radial functions. The radial functions were generated as the numerical solutions of a model scattering problem based on the isotropic expansion of the target potential and subject to R-matrix boundary conditions. The functions were then Schmidt orthogonalised to the molecular orbitals of the target. For further details see Salvini (1983) and Tennyson *et al* (1984).

The second summation in equation (1) consists of L^2 correlation terms in which all $N+1$ electrons occupy target molecular orbitals. In the simple close-coupling (CC) or static exchange (SE) model, configurations are selected in which the scattered electron occupies a target virtual molecular orbital with the appropriate symmetry, while no excitation of the remaining electrons is permitted. These correlation configurations account for short-range high-angular-momentum effects which would otherwise be neglected due to the truncation of the continuum orbital partial-wave expansion.

Polarisation effects, not given by the close-coupling expansion, are included in the close-coupling plus polarisation (CCP) and static exchange plus polarisation (SEP) models by allowing single-particle excitations of the target—giving two-particle, one-hole (2p, 1h) configurations. In the CC calculations, only (2p, 1h) excitations of the ground-state configuration were included so that no double excitations of the target were allowed.

3. One-state calculations

In the present calculations, the NO $^2\Pi$ target, at its equilibrium separation of 2.1747 a_0, was represented by the 24 STO SCF (Slater-type orbitals, self-consistent field) wavefunction of Cade and Huo (1975). This was augmented by numerically defined continuum orbitals with $l \leq 5$. Solutions of our model problem with energies of 6 Ryd or less were included, giving about nine numerical functions for each partial wave. Test calculations with both Σ and Π symmetries, which included (*a*) partial waves with $l \leq 8$ and (*b*) two extra functions per partial wave, suggested that this basis gives a good representation of the continuum for scattering energies below 2 Ryd.

Figure 1 shows the variation of the total eigenphase with scattering energy for the $^1\Pi$ and $^3\Pi$ symmetries. Results are presented for four different approximations. The lowest eigenphases are given by the SE-σ model which neglects both polarisation and coupling to continuum orbitals with δ symmetry. Secondly, both σ and δ orbitals are included in the SE model. The analogous results are given for the SEP model calculations which have all possible (2p, 1h) excitations in which a target electron is excited from the 4σ, 5σ, 1π or 2π molecular orbitals.

The results in figure 1 indicate that, particularly at higher energies, it is essential that the δ continuum is included too. Significant errors are introduced if coupling to continua of either symmetry or polarisation effects are neglected. We also note the similarity of the singlet and triplet curves, which shows that the spin coupling between target and scattering electrons is weak within the one-state model.

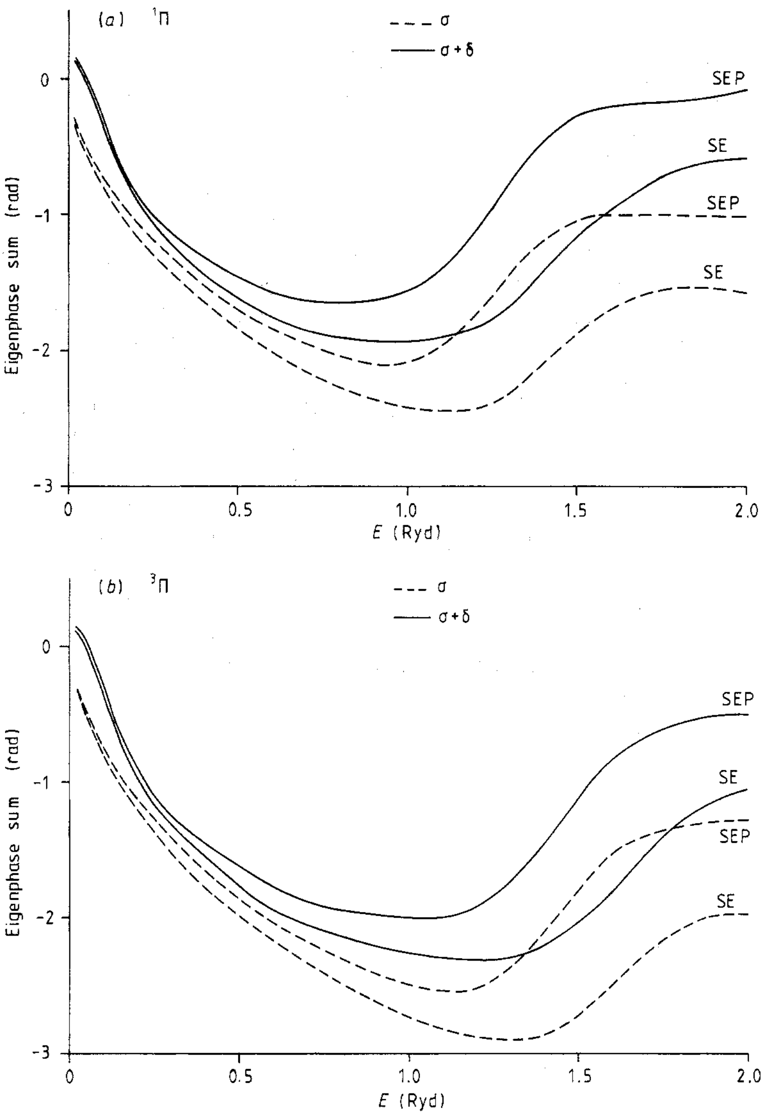

Figure 1. Eigenphase sums in radians as a function of scattering energy in rydbergs for e-NO scattering in (*a*) $^1\Pi$ and (*b*) $^3\Pi$ symmetries. One-state results for various models (see text for details).

Stronger coupling might be expected in the symmetries which support low-lying long-lived states of NO^-. Table 1 compares resonance parameters calculated for the three low-lying states of NO^-. Only in the $^1\Delta$ state is it necessary to consider coupling to the continuum for more than one symmetry. However, neglect of the ϕ continuum orbitals introduces only a small shift in the resonance position (about 0.004 Ryd in both SE and SEP models) and widths. This is a consequence of the angular momentum barrier which prevents the lowest partial wave with this symmetry, $l = 3$, penetrating into the resonance region.

Conversely, the resonance positions are very sensitive to the inclusion of polarisation effects, with shifts in the resonance positions of about 0.02 Ryd at this level of

Table 1. Breit–Wigner resonance parameters for the low-lying states of NO^-: one-state calculations for internuclear separation of 2.1747 a_0.

Symmetry	E_{res} (Ryd)	Γ_{res} (Ryd)	Model
$^1\Sigma^+$	0.211	0.105	SE
	0.197	0.089	SEP
$^1\Delta$	0.151	0.060	SE-π
	0.147	0.069	SE-$\pi+\phi$
	0.135	0.047	SEP-π
	0.131	0.053	SEP-$\pi+\phi$
$^3\Sigma^-$	0.090	0.026	SE
	0.066	0.013	SEP

calculation. Test calculations which expanded the set of orbitals available for constructing the optical potential suggested that this potential was poorly converged at the level given in table 1. This was in contrast to the SE calculations which proved to be insensitive to increasing the virtual orbitals available for correlation effects.

It would be desirable to improve systematically the optical potential so that convergence could be demonstrated. However, experience with the low-lying resonances in N_2 (Schneider and Collins 1984) has shown that it is possible to overcorrelate the negative ion relative to the neutral target. As this calculation, in common with most electron–molecule scattering calculations, uses a Hartree–Fock target wavefunction, this possibility cannot be ignored. Furthermore, the use of large sets of target virtual orbitals has led to problems with linear dependence of our numerical continuum functions (see, for example, Tennyson and Noble 1985).

An alternative method of including polarisation effects is via the explicit inclusion of electronic states in the close-coupling expansion, equation (1). As NO has several low-lying electronically excited states, this would appear a particularly appropriate procedure for this system.

4. Coupled-states calculations

The lowest electronically excited states of NO are the a $^4\Pi$ and b $^4\Sigma^-$ (Radloff and Freedman 1979); above these lie many doublet states with increasing Rydberg character (Miescher and Huber 1976). In order to limit the number of states in the close-coupling expansion, only those given by the lowest single-particle excitations of the ground-state configuration, $5\sigma^2 2\pi^1 \rightarrow 5\sigma^1 2\pi^2$ and $1\pi^4 2\pi^1 \rightarrow 1\pi^3 2\pi^2$, were considered. As higher excited states are increasingly Rydberg-like, the close-coupling expansion was further restricted by including only the lowest state of a particular symmetry. Finally, the $^2\Phi$ state was dropped from the expansion as this couples to the symmetries of interest only via partial waves with relatively high m. This led to a set of six low-lying states of NO, details of which are given in table 2.

The energies given in table 2 and corresponding wavefunction were obtained for the excited states by single-particle excitation of the target ground state. This procedure, similar to that used by Fliflet and McKoy (1980), tends to overestimate the threshold energies. While accurate thresholds are important for inelastic processes, here we are

Table 2. Energies, configurations and couplings for the six low-lying states of NO explicitly included in the coupled-states calculations.

Target state	Configuration $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2)$	Energy (Hartree)	Number of partial waves[a] for scattering state $^1\Pi$	$^3\Pi$	$^3\Sigma^-$	$^1\Delta$	$^1\Sigma^+$
$^2\Pi$	$5\sigma^2 1\pi^4 2\pi^1$	−129.283 65	10	10	5	5[b]	5
$^4\Pi$	$5\sigma^2 1\pi^3 2\pi^2$	−129.079 62	-	10	5	-	-
$^4\Sigma^-$	$5\sigma^1 1\pi^4 2\pi^2$	−129.068 18	-	5	6	-	-
$^2\Delta$	$5\sigma^1 1\pi^4 2\pi^2$	−128.974 85	5[b]	5[b]	4	6[c]	4
$^2\Sigma^-$	$5\sigma^1 1\pi^4 2\pi^2$	−128.931 90	5	5	6	4	-
$^2\Sigma^+$	$5\sigma^1 1\pi^4 2\pi^2$	−128.926 95	5	5	-	4	6
Total number of channels			25	40	26	19	15

[a] All $l \leq 5$.
[b] Coupling to the $m = 3$ (ϕ) continuum neglected
[c] Coupling to the $m = 4$ continuum neglected.

concerned with elastic scattering below the lowest electronic excitation threshold. In the present work the excited states can be thought of as fulfilling a role similar to the pseudostates commonly used in atomic calculations.

Coupled-states calculations were performed using a continuum basis set containing functions of σ, π and δ symmetry with $l \leq 5$, which gave a total of 102 continuum functions. Functions with $m \geq 3$ were not included in our basis as the one-state calculations indicated that the effect of these is small in the low-energy region considered here. Calculations were performed with the CC model which only allowed for polarisation through the close-coupled expansion, analogous to the SE model for a one-state calculation, and the close-coupling plus polarisation (CCP) model which allowed for additional polarisation effects through (2p, 1h) excitations of the ground state, analogous to the SEP model.

Figure 2 compares six-state calculations, with and without the additional polarisation, and with the one-state SEP-$\sigma + \delta$ calculation of the previous section. Only energies below the first electronic excitation threshold are considered. The one-state and six-state calculations are in good qualitative agreement, although the systematically higher eigenphases in the six-state calculations suggest that some polarisation effects were indeed neglected in the one-state calculations. Conversely the CC and CCP results are nearly indistinguishable on the scale of the figure, unlike the one-state calculations where the inclusion of polarisation resulted in a significant shift in the eigenphase sum. One explanation for this is that our coupled-states expansion gives a good representation of the polarisation effects, making the additional optical potential unnecessary, although we cannot exclude the possibility that our (2p, 1h) configurations do not represent all the remaining polarisation effects. Finally, we note that the $^1\Pi$ and $^3\Pi$ curves still mimic each other; this is despite the possibility of extra coupling by the $^3\Pi$ state to the two low-lying target quartet states.

Table 3 presents resonance parameters for the low-lying states of NO^- calculated in the six-state approximation. For comparison a summary of the experimental results is also given. The six-state resonance positions and widths are significantly lower and narrower than the best one-state results (see table 1) and are again less sensitive to polarisation effects.

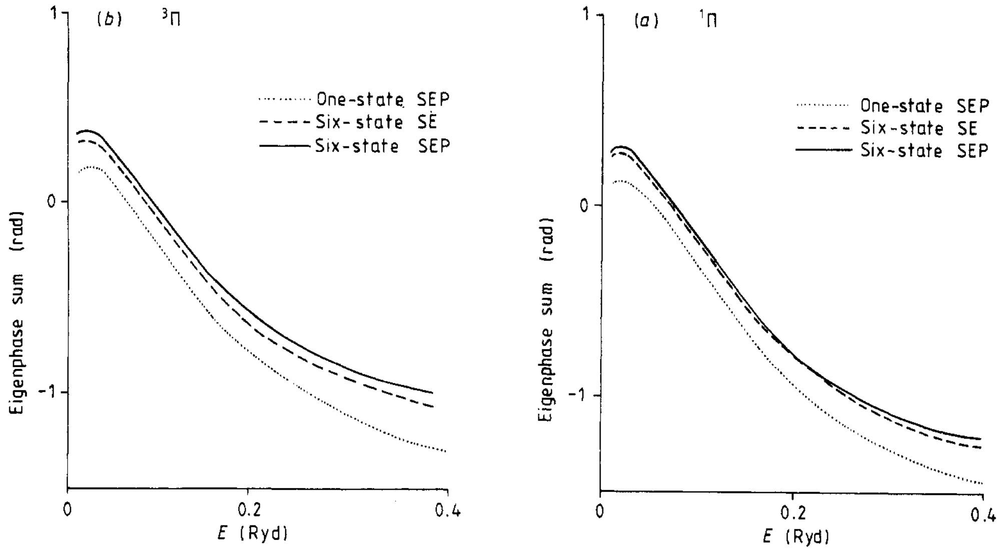

Figure 2. Eigenphase sums in radians as a function of scattering energy in rydbergs for e-NO scattering in (*a*) $^1\Pi$ and (*b*) $^3\Pi$ symmetries. Comparison of one-state and six-state results. The six-state SE (CC) and SEP (CCP) results are nearly indistinguishable on this scale.

Table 3. Breit-Wigner resonance parameters for the low-lying states of NO^-: six-state calculations for internuclear separation of $2.1747a_0$.

Symmetry	E_{res} (Ryd)	Γ_{res} (Ryd)	Model
$^1\Sigma^+$	0.170	0.069	CC
	0.169	0.068	CCP
	>0.15		a
	0.082		b
$^1\Delta$	0.102	0.030	CC
	0.101	0.029	CCP
	>0.15		a
	0.057		b, c
$^3\Sigma^-$	−0.035		CC
	−0.038		CCP
	−0.004		a, d
	−0.002		b, c

[a] Zecca *et al* (1974).
[b] Tronc *et al* (1975).
[c] Burrow (1974).
[d] Siegel *et al* (1972).

One consequence of the stabilisation of the NO^- states relative to the NO ground state is that the lowest state, with $^3\Sigma^-$ symmetry, is now predicted to be bound. An estimate of the binding energy was obtained by performing a negative-energy scattering calculation following the method of Ohja and Burke (1983).

As we have only performed fixed-nuclei calculations, comparisons with the vibrationally resolved experimental results must be made with caution. In particular, the increased bond length of the NO^- states relative to the NO ground state (Teillet-Billy and Fiquet-Fayard 1977) should result in smaller observed adiabatic energies than the vertical excitation energies we calculate. Additionally, the experimental vibrational thresholds also include contributions from the change in zero-point energy between NO and NO^-. However, there is good qualitative agreement between our results and the interpretation placed upon their observations by Tronc *et al* (1975), who were able to see vibrational levels belonging to all three NO^- states in the complicated resonance structure of low-energy e-NO scattering. Conversely our results suggest that the explanation in terms of lifetimes and energies, given by Zecca *et al* (1974) and Burrow (1974), for not observing resonance effects due to all three low-lying states of NO^- is not correct. Indeed, we predict similar lifetimes for the $^1\Delta$ and $^1\Sigma^+$ resonances contrary to the suggestion by Burrow that the $^1\Sigma^+$ state is so short-lived that it is not observed in scattering experiments.

5. Conclusions

In summary, we have performed low-energy electron impact calculations for NO, using up to six target states in a close-coupling expansion. Inclusion of polarisation in one-state calculations results in large changes in the calculated eigenphases. This can be attributed to the presence of many low-lying excited states of NO. Couplings induced by the degenerate NO target are found to be significant between σ and δ continua, but less important at low energies between π and ϕ continua.

Our six-state calculations appeared stable to the inclusion of further polarisation effects via an optical potential, suggesting that indeed polarisation is well represented in this model. The positions obtained for the three lowest states of NO^-, namely $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$, support the results inferred from the experiment by Tronc *et al* (1975) rather than the earlier interpretations of Zecca *et al* (1974) and Burrow (1974). Finally, we note that a method is currently under development which should allow for the routine inclusion of many target states in the close-coupling expansion (Burke and Noble 1985, 1986).

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