Potential energy curves of molecular nitrogen for singly and doubly ionized states with core and valence holes

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The accurate theoretical description of potential energy curves of molecular ions is essential for interpreting and predicting coupled electron-nuclear dynamics. In this work, we calculate potential energy curves of single and double ionized molecular nitrogen in an *ab initio* manner, using the multi configurational self-consistent field method. An accurate representation of these potential energy curves for inter-nuclear distances close to the dissociation limit is not trivial for molecular nitrogen, especially for the states with an inner valence or core holes. Herein, the double loop optimisation scheme within the multi configurational method is implemented to obtain the correct ionization and dissociation energies. The difference in the potential energy curves when using localized versus delocalized molecular orbitals are also addressed. These potential curves are of significance for future calculations of the interplay between photoionization and Auger spectra during the break-up of molecular nitrogen when interacting with intense free electron lasers.

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I. INTRODUCTION

The advancement of experimental techniques in X-ray[1] and extreme ultraviolet spectroscopy[2,3] has facilitated an in depth study of electron dynamics in atomic[4,5] and molecular systems[6,7] as well as coupled electron-nuclear dynamics in molecules.[8,9] Accurate theoretical methods are needed to interpret and utilise the results obtained from high precision XUV measurements. Intense X-ray sources, e.g., synchrotrons or X-ray free energy lasers (FEL) are capable of inducing ionization from inner-shell electrons of atoms and molecules. The ionization of inner shell electrons gives rise to an interplay between ionization by single photon absorption and Auger processes. Most studies addressing the interaction of molecules with FEL pulses do not account for the nuclear motion. This is due to the difficulty involved in computing the potential energy curves (PEC) for molecules with core hole states. The dissociation of the molecule is taken into account mostly in a phenomenological way through additional terms in the rate equations employed to compute the resulting atomic ion yields.[10] In this work, we compute potential energy curves of singly and doubly ionized molecular nitrogen. This will allow future studies to explicitly account for the nuclear motion when a molecule interacts with an FEL-pulse.[11,12]

Several theoretical studies have computed potential energy curves of singly and doubly ionized states of N_2 employing quantum chemistry packages.[13–17] These studies compute the PECs for N_2 states with one or two outer valence electrons missing or with one core hole. These computations have been carried out using a multi-configurational self consistent field (MCSCF) method.[18–20] To achieve better accuracy for the PECs of states with outer valence holes, in addition to MCSCF, some theoretical studies employ the multi-reference configuration interaction (MRCI) method.[21–23] In this work, for completeness, we also compute the PECs of N_2 states with one or two outer valence electrons missing. In contrast, there are a few studies computing the PECs for N_2 states with an inner valence[24] or core electron missing.[25–27] The computation of the PECs of these latter states is not trivial. The reason is that there are several states with lower energy that have the same symmetry as the state of interest that has an inner valence or core hole. This results in variational collapse[28] to the lowest energy state during optimization of the orbitals and the coefficients in methods like MCSCF.[28,29] In previous studies, the computation of the PECs of N_2 with a single core hole[25–27] has been carried out in a two-step optimization process. In the first step, the valence orbitals are optimized with MCSCF, while the core orbitals are kept frozen. In the second step, it is the valence orbitals that are kept frozen, while we optimize with MCSCF the core ones. This two-step process was introduced and implemented by Rocha[30] to obtain the PECs for the ionized states of the CO molecule. A similar two-step optimisation process has also been employed by Carravetta *et al*[31] to compute the energy at the equilibrium internuclear distance, rather than PECs, of N_2 states with multiple core holes. Herein, first, we compute the PECs of N_2 states with one or two outer valence electrons missing. We do so for completeness and to compare our results with existing ones. Most importantly, employing this two-step optimization process, we also compute the PECs of N_2 states with one inner valence hole or two core hole states. To our knowledge, currently, there are no studies of the PECs for these latter singly and doubly ionized states of N_2.

II. METHOD

In what follows, we describe the computation of the potential energy curves of singly and doubly ionized states of N_2 that involve all possible combinations of electrons missing either from valence or core orbitals. The ground state electronic configuration of N_2 is ($1\sigma_g^2$ $1\sigma_u^2$ $2\sigma_g^2$ $2\sigma_u^2$ $1\pi_{ux}^2$ $1\pi_{uy}^2$ $3\sigma_g^2$). The $1\sigma_g$ and $1\sigma_u$ are core orbitals, $2\sigma_g$ is an inner valence orbital[32], while the rest are referred to as valence ones. The MCSCF[33] method combines the configuration interaction (CI) with the self-consistent field (SCF) method. The former optimizes the coefficients of the Slater determinants, while SCF optimizes the orbitals involved in the Slater determinants. Moreover, MCSCF[33–36] involves a combination of Slater determinants that account for all possible electronic excitation of the molecule under consideration.

In the current work, we employ the complete active space (CAS) variant of the MCSCF method, which we refer to as CASSCF.[37,38] The CASSCF method involves active orbitals with an occupancy, n, that ranges from $0 < n < 2$, and inactive unoccupied orbitals. In the current work, we consider 10 active orbitals $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $3\sigma_g$, $1\pi_{gx}$, $1\pi_{gy}$, $3\sigma_u$, where the first seven correspond to doubly occupied orbitals and the last three have weak occupation in the ground state of N_2. The three virtual orbitals that we select as active orbitals are the lowest in energy and have similar energies, all other virtual orbitals have much higher energies. Hence, the selection is all electron core and full valence active space. This CASSCF method allows for an accurate computation of the energy of an ionized state of N_2 as a function of the internuclear distance, since it accounts for all possible electronic excitations to three virtual orbitals. Here, we use the Molpro[39,40] quantum chemistry package to perform the CASSCF calculations. To improve the initial description of the orbitals of ionized states of N_2, we run a CASSCF with ten active orbitals for the ground state of N_2. In addition, for the computation of N_2 states with one valence hole, we employ the augmented Dunning correlation consistent quadruple valence basis set (aug-cc-pVQZ)[41], while we use the quintuple zeta basis set (cc-pV5Z)[41] for states with two valence holes. Such basis sets have been previously employed to accurately account for electronic correlation in singly and doubly ionized states.[23,24]

Finally, to obtain the PECs of N_2 states with one or two valence holes we optimize all ten orbitals with the CASSCF method. In contrast, we compute the PECs of N_2 states with one or two core holes by employing a two-step optimization process, similar to the two-step process in Ref. 30. Specifically, first, we freeze the two core orbitals $1\sigma_g$ and $1\sigma_u$ and optimize with CASSCF the remaining eight active ones. Then, we freeze the five occupied orbitals optimized in the first step and optimize with CASSCF the remaining two core and three virtual orbitals $1\pi_{gx}$, $1\pi_{gy}$ and $3\sigma_u$. In our calculations, we have checked that it suffices to perform this two-step optimization process once or twice in order for the energy of the N_2 ionized states under consideration to converge.

III. RESULTS AND DISCUSSION

In what follows, we discuss our results for the potential energy curves, first, for singly ionized states and then for doubly ionized states of N_2, with valence and/or core electrons missing.

A. Singly ionized states

1. *Valence states*

In Figure 1(a), we present the potential energy curves that we obtain using the CASSCF method for the ground state (black-dashed) and the three lowest energy singly ionized states of N_2. We obtain the PECs up to the distance corresponding to the dissociation limit of 4Å of N_2. The latter states are obtained when removing an electron from the $3\sigma_g$ (blue-dashed), $1\pi_u$ (grey-dashed) or $2\sigma_u$ (brown-dashed) molecular orbital. In what follows, we refer to these singly ionized states either as $3\sigma_g^{-1}$, $1\pi_u^{-1}$ (x or y) and $2\sigma_u^{-1}$ or by the symmetry of the respective state ($1^2\Sigma_g^+$, $1^2\Pi_u$, $1^2\Sigma_u^+$) according to the $D_{\infty h}$ symmetry point group. As expected, the PECs of the $3\sigma_g^{-1}$, $1\pi_u^{-1}$ (x or y) and $2\sigma_u^{-1}$ states lie above the PEC of the ground state of N_2 and converge to the same

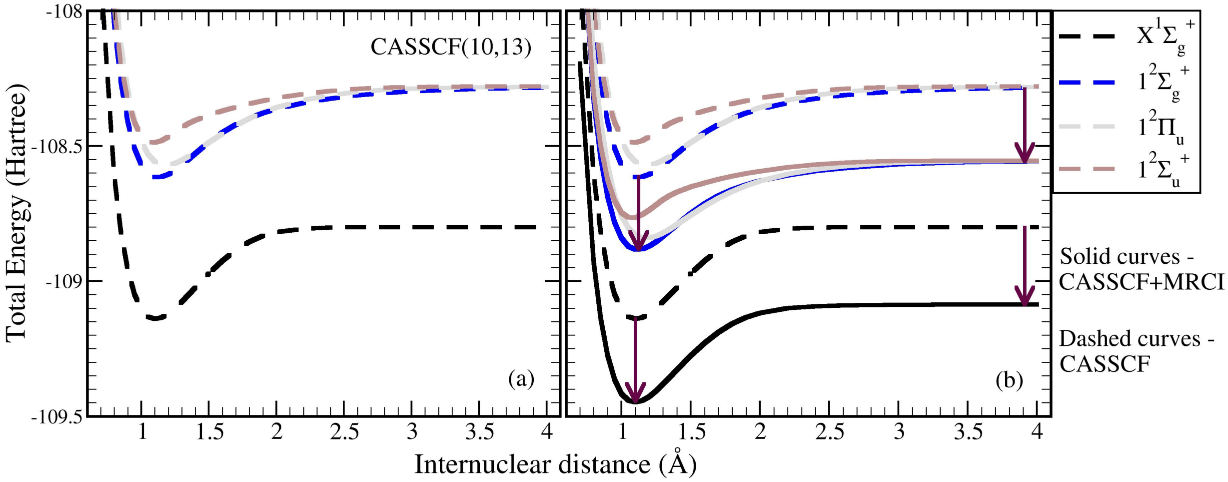

FIG. 1. a) Potential energy curves for the ground state ($X^1\Sigma_g^+$) and the three lowest energy singly ionized states of N_2, i.e., $1^2\Sigma_g^+$ ($3\sigma_g^{-1}$), $1^2\Pi_u$ ($1\pi_u^{-1}$ (x or y)) and $1^1\Sigma_u^+$ ($2\sigma_u^{-1}$). These curves are obtained with CASSCF. The total energy of each state is expressed in units of Hartree, while the internuclear distance is expressed in Å. b) The PECs of the same four states of N_2 as in a, obtained with CASSCF+MRCI (solid curves). For comparison, we also show the PECs obtained with CASSCF (dashed curves).

dissociation limit. We find our results for these four states of N_2 to be in good agreement with those reported by Nagy *et al*[13] for internuclear distances in the interval (0.8 - 1.6Å), which are considered in Ref. 13.

To obtain more accurate PECs for the ground and three lowest energy singly ionized states of N_2, we employ the MRCI[42–44] method using the optimized orbitals obtained from the CASSCF method and employing the same active space. MRCI allows for single and double electronic excitation to nearly all virtual states in contrast to CASSCF which allows for all possible electronic excitation to three virtual states. As a result, MRCI improves the description of the electron-electron repulsion. In Figure 1(b), we plot the thus obtained more accurate PECs of the four states of N_2 with our results in Figure 1(a) obtained using only CASSCF. As expected, we find that the PECs obtained with the CASSCF+MRCI method have lower energies. However, we find that the equilibrium internuclear distance, the depth of the potential well and the dissociation limit of each PEC remains nearly the same when employing either the CASSCF or the CASSCF+MRCI methods. In addition, we find that our results for the PECs for the ground and three lower singly ionized states of N_2 using the CASSCF+MRCI methods, are in excellent agreement with the results obtained in Ref. 22. We also find that the dissociation limit of the ground state of N_2 is 9.82 eV and of the three lowest singly ionized states is roughly equal to 24.3 eV, which are in very good agreement with the experimentally obtained ones of 9.78 eV[45] and 24.31 eV[46], respectively.

Next, we compute the PEC of the $2\sigma_g^{-1}$ singly ionized state of N_2 resulting from the removal of an inner valence ($2\sigma_g$) electron. As already pointed out in the introduction, this is not a trivial task. The reason is that besides the desired state there are several other states with the same symmetry (Σ_g^+) and lower energy. To obtain the desired singly ionized state, we proceed as follows. During the CASSCF calculation, we ensure that Molpro[39,40] computes a sufficient number of Σ_g^+ symmetry states as a function of the internuclear distance. We identify the desired singly ionized state of N_2 by selecting the Σ_g^+ state that has an occupation number equal to 1 for the $2\sigma_g$ state at the equilibrium geometry. We find that the $2\sigma_g^{-1}$ state of N_2 corresponds to the 6^{th} lowest energy state of Σ_g^+ symmetry, in accord with Ref. 16. This state (red-dashed curve) is plotted in Figure. 2. For comparison we also plot the ground and the three lowest energy singly excited states of N_2. We find, that the $2\sigma_g^{-1}$ state is repulsive in nature. This is in contrast to the other three PECs which have an energy minima as a function of the internuclear distance. In addition, we find that the vertical ionization energy from the ground state of N_2 to the $2\sigma_g^{-1}$ ionized state is 38.3 eV. This compares very well with the value of 40.5 eV reported by Aoto *et al.*[16] that employ a CASSCF method similar to the one employed in the current work. Our result for the vertical ionization energy also compares well with the value of 36.9 eV reported by Kornilov *et al.*[24] that do not employ CASSCF method.

The results presented above for the PECs of the ground state and singly ionized states of N_2 were obtained using the aug-cc-pVQZ basis set. To test our results for convergence, we also compute the same PECs of these states employing the aug-cc-pVTZ basis set. In Table I, we show the vertical ionization energy (VIE), adiabatic ionization energy (AIE) and the dissociation energy (DE) of these PECs obtained using the two basis sets. The VIE is the energy difference between the ground state and each singly ionized state of N_2 at the equilibrium distance of N_2. The AIE is the difference between the energy minima of N_2 and each one of the singly ionized states. DE corresponds to the final energy of each singly ionized state at the internuclear distance of 4Å. Table I shows that we obtain similar results when employing the two different basis sets both in the CASSCF and the CASSCF+MRCI methods. We find that our results are in excellent agreement with the available experimental results for the VIE, AIE and DE obtained in Ref. 46. Moreover, our results for the AIE agree very well with the theoretical results obtained in Ref. 22

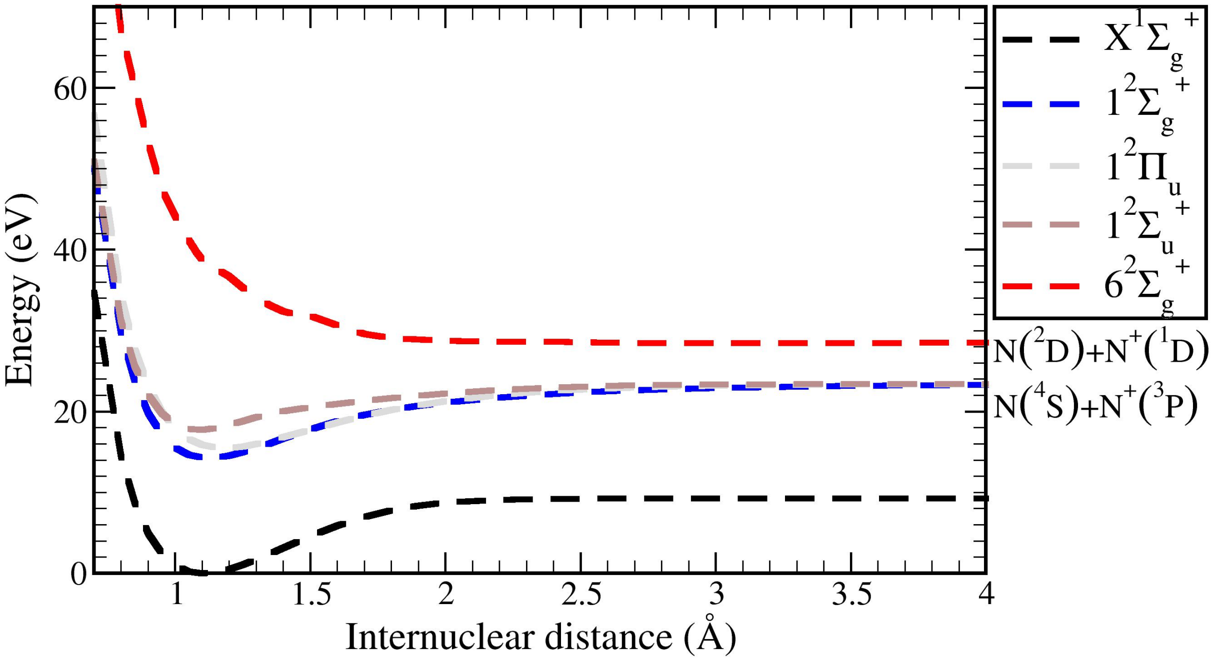

FIG. 2. Potential energy curves of the $2\sigma_g^{-1}$ state of N_2 (red-dashed curve) calculated using CASSCF. For comparison, we also show the ground state (black-dashed curve), $3\sigma_g^{-1}$ (blue-dashed), $1\pi_u^{-1}$ (grey-dashed) and $1^1\Sigma_u^+$ (brown-dashed) states as in Figure 1(a). The PECs are plotted with respect to the ground state energy of N_2. The dissociation limits are also shown.

when we employ CASSCF+MRCI as the authors in the latter reference. Finally, the dissociation energies we obtain using both CASSCF and the CASSCF+MRCI are in good agreement with the results obtained in Refs. 24,46 and 16.

2. Core states

In this section, we present the PECs of the singly ionized states of N_2 with one core hole. As discussed previously, we implement a two-step optimization process with restricted core occupancy to compute these states. It is pertinent to mention here that the main motivation of this work is to obtain the electron spectra generated by an FEL pulse also taking into account the explicit nuclear motion. In a previous work,[11] where we treated the nuclear motion phenomenologically through rate equations, we obtained accurate electron spectra using molecular orbitals of N_2, i.e.

TABLE I. Basis set comparison for valence singly ionized states. DE is computed at an internuclear distance of 4 Å. All energies are expressed in eV.

	Electronic configuration	aug-cc-pVTZ		aug-cc-pVQZ		Other calculations	Exp.
		CAS	CAS+MRCI	CAS	CAS+MRCI		
VIE	$3\sigma_g^{-1}$	14.31	15.35	14.30	15.39	-	15.58[a]
	$1\pi_u^{-1}$	15.87	15.52	15.86	16.84	-	16.926[a]
	$2\sigma_u^{-1}$	17.47	18.53	17.75	18.60	-	18.751[a]
	$2\sigma_g^{-1}$	36.64	-	38.22	-	40.5,[b] 36.9[c]	-
AIE	$3\sigma_g^{-1}$	14.30	15.34	14.29	15.39	15.347[d]	15.58[a]
	$1\pi_u^{-1}$	15.49	15.52	15.50	16.55	16.49[d]	16.693[a]
	$2\sigma_u^{-1}$	17.47	18.53	17.74	18.59	18.558[d]	18.751[a]
DE	$3\sigma_g^{-1}$	23.25	24.14	23.29	24.28	24.293[b]	24.31[a]
	$1\pi_u^{-1}$	23.32	24.18	23.37	24.32	24.293[b]	24.31[a]
	$2\sigma_u^{-1}$	23.34	24.22	23.41	24.36	24.293[b]	24.31[a]
	$2\sigma_g^{-1}$	28.35	-	28.51	-	28.578,[b] 31.9[c]	-

[a] Ref. 46

[b] Ref. 16

[c] Ref. 24

[d] Ref. 22

delocalized orbitals. This is in accord with high resolution electron spectroscopy experiments which measured the energy splitting of the $1\sigma_g$ and $1\sigma_u$ molecular core-hole states of N_2.[47–50] Given the above, here, we obtain the PECs of delocalized molecular core hole states of N_2. In addition, to compare with previous studies,[26,27] we calculate the PECs for core hole states that are localized on a given atomic site of N_2.

Following previous work[26,27], we calculate the PECs for the singly ionized states of N_2 with one core hole that correspond to different types of delocalised orbitals. For one type, we restrict the occupancy of the delocalized molecular orbitals $1\sigma_g$ or $1\sigma_u$ to be equal to 1, while the occupancy of the other is equal to 2. For the second type, we restrict the occupancy for the pair of $1\sigma_g$ and $1\sigma_u$ orbitals to be equal to 3; we denote the resulting delocalized orbitals by $1\sigma_g'$ and $1\sigma_u'$. Moreover, to compute the PECs using localized orbitals, we proceed as follows. As for all our

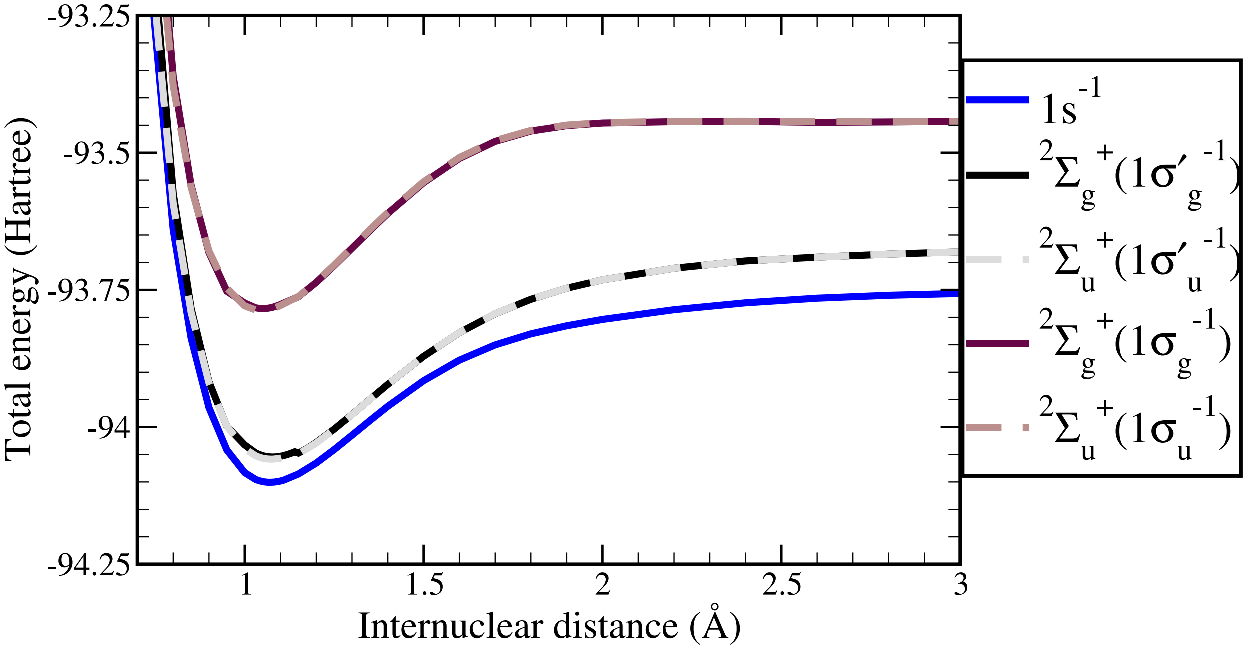

FIG. 3. The PECs of singly ionized states of N_2 with one core hole.

other calculations, we start by obtaining the ground state of N_2 employing CASSCF. However, since our goal is to obtain localized orbitals for the core hole states, we assign the C_{2v} instead of the $D_{\infty h}$ point symmetry group. To obtain the core localized orbitals, we apply the Pipek-Mezey localization technique[51] in Molpro to the CASSCF molecular orbitals of the ground state of N_2. We label the resulting localized orbitals by 1s. Finally, we restrict the occupancy of either one of the localized core orbitals to 1, freeze this orbital, and apply CASSCF to optimize the remaining active orbitals.

Figure 3 shows the PECs of the singly ionized states of N_2 with one core hole. For better accuracy,[53] we use the aug-cc-pCVQZ[54] basis set which is a larger core-augmented as compared to the aug-cc-pVQZ basis set we employed for valence hole states. We find that the PECs of the core localised orbital have lower energy than the PECs for the delocalised orbital sets. Moreover, we find that the PECs of the delocalized orbitals $1\sigma_g'$,$1\sigma_u'$ lie close to each other and the same holds for the PECs for the $1\sigma_g$,$1\sigma_u$. However, the PECs of the $1\sigma_g'$,$1\sigma_u'$ differ from the $1\sigma_g$,$1\sigma_u$ and have different dissociation limit. In Figure 4, we compare our results for the PECs of states with one core hole (solid curves) with those obtained in Ref. 27 (dashed curves). As in Ref. 27, we plot the PECs with respect to the minimum energy of the localized core hole state $1s^{-1}$. It is clearly shown that all the PECs quantitatively agree with those reported previously.[27] The difference in

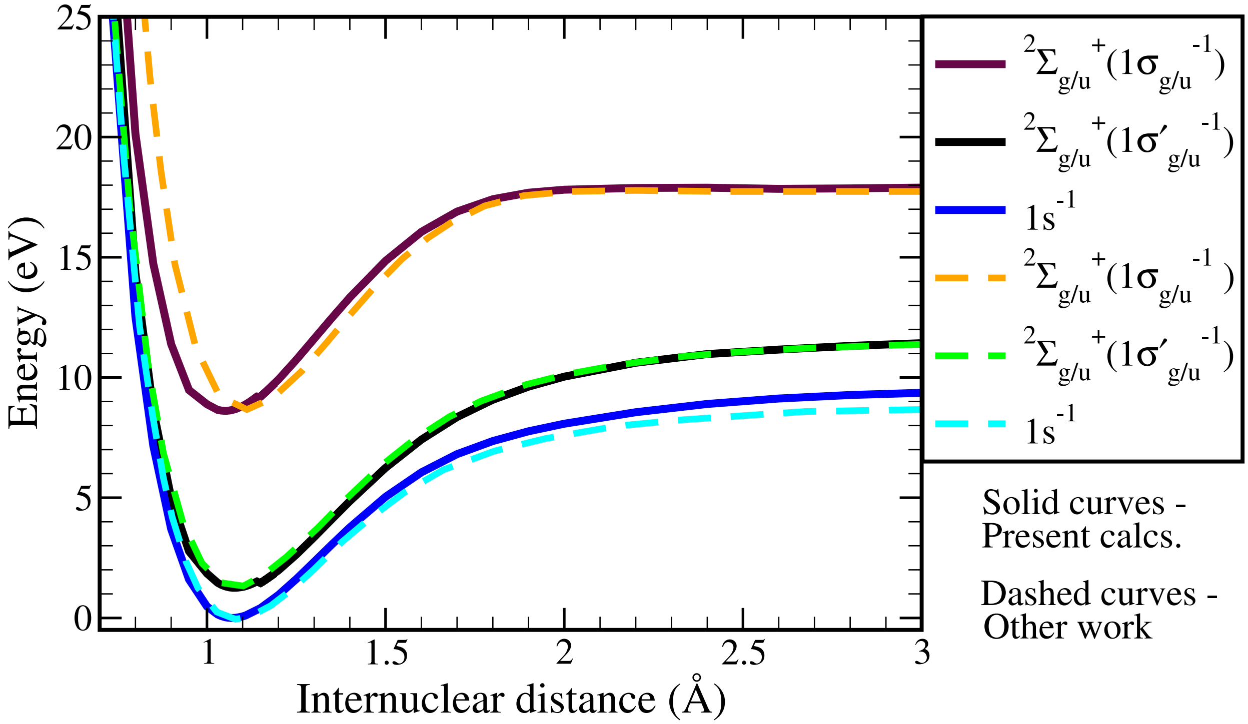

FIG. 4. The PECs for the singly ionized states of N_2 in comparison with previous work. The PECs depicted by dashed curves are taken from Ref. 27.

the current work is that the energy minimum of the PECs of $1\sigma_g$,$1\sigma_u$ is shifted to shorter bond length.

To test for convergence, we compute the PECs of the singly ionized states of N_2 with a core hole employing different basis sets. In Table II, we show our results for the AIE and the depth of the potential well (D_e) using the aug-cc-pCVQZ basis set and a smaller valence triple-zeta basis, aug-cc-pVTZ[41]. The depth of the potential well is defined as the energy difference between the dissociation limit and the energy minimum of the PEC. We find that our results are similar for both basis sets. Moreover, we find that our results for AIE and D_e agree well with the results obtained in the theoretical studies in Ref. 27 where a CASSCF method is employed but with a 6-311G* basis set. Our result for the AIE of the $1\sigma_g'^{-1}$,$1\sigma_u'^{-1}$ states have excellent agreement with experimentally obtained results.[52] For instance, the difference of 110 meV in energy between the g and u symmetry states, observed experimentally (see Table II) is reproduced very well by our results.

TABLE II. Basis set comparison for singly ionized states with core hole. All energies are expressed in eV.

	Electronic configuration	aug-cc-pVTZ	aug-cc-pCVQZ	Previous work[a]	Exp.[b]
AIE	$\sigma_g'^{-1}$, $\sigma_u'^{-1}$	410.28, 410.16	410.06, 409.95	410.8, 410.9	409.93, 409.82
	σ_g^{-1}, σ_u^{-1}	417.59, 417.49	417.42, 417.33	418.2, 418.3	-
	$1s^{-1}$	409.50	409.26	409.5	-
D_e	$\sigma_g'^{-1}$, $\sigma_u'^{-1}$	10.43, 10.54	10.42, 10.53	10.31	-
	σ_g^{-1}, σ_u^{-1}	9.35, 9.42	9.40, 9.44	9.00	-
	$1s^{-1}$	9.36	9.33	8.81	-

[a] Ref. 27

[b] Ref. 52

B. Doubly ionized states

The ionization of two electrons from any one of the molecular orbitals of N_2 results in several ionized states. The final number of doubly ionized states and hence, of PECs increases since we also take the spin into account. If the two electrons are removed from the same molecular orbital the resulting ionized state is a singlet one, while if the two electrons are removed from two different molecular orbitals the resulting states can be either singlet or triplet.

1. Valence states

To generate doubly ionized states of N_2 with two holes in the valence orbitals, we apply the CASSCF method using the cc-pV5Z basis set. For ionized states of N_2 with two outer valence holes, we apply the CASSCF method to optimize all ten active orbitals, as we previously did for the ionized states of N_2 with one valence hole. To compute the ionized states of N_2 with at least one inner valence or core hole, we implement the two-step optimization process that we had previously employed to obtain the ionized states of N_2 with a single core hole. We apply the two-step optimization process, within the framework of CASSCF. That is, we first freeze the orbitals where the two electrons are ionizing from and optimize the remaining eight active orbitals. In the second step, we freeze the previously optimized five active occupied orbitals and proceed to

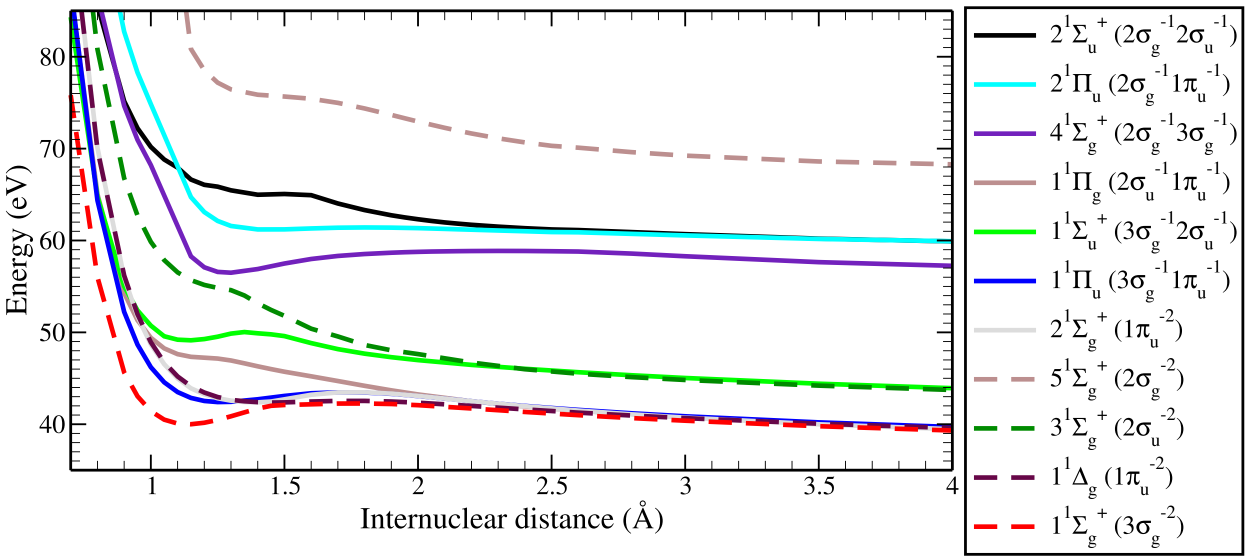

FIG. 5. PECs of singlet doubly ionized states of N_2 with two valence holes. Dashed (solid) curves represent states where both electrons are removed from the same (different) orbitals.

optimize the molecular orbitals with missing electrons as well as the three virtual orbitals. We repeat this process until convergence is achieved.

In Figure 5 we show the PECs of singlet doubly ionized states of N_2 with two valence holes. We find that all PECs converge to five distinct dissociation energies at 4 Å. All PECs that have a dissociation energy between 38−44 eV correspond to two electrons missing from outer valence orbitals. Using the energies by Iwayama *et al.*[32] of the atomic ion states that corresponds to final dissociation products of N_2, we find that doubly ionized states of N_2 with two outer valence holes undergo symmetric breaking to $N^+ + N^+$. We also find that the states $4^1\Sigma_g^+$ and $5^1\Sigma_g^+$ undergo an asymmetric dissociation to N^{2+} + N, while the states $2^1\Pi_u$, $2^1\Sigma_u^+$ undergo symmetric break up. In Figure 6, we plot the PECs of triplet doubly ionized states of N_2 with two valence holes. The PECs of all triplet N_2 states with two outer valence holes have a symmetric bond breaking. The reason is that these triplet states have a DE around 39 eV which can only be accessed by a symmetric bond breaking.

To the best of our knowledge, the PECs of the doubly ionized states of N_2 with at least one inner valence hole have not been previously computed. However, there is an experimental prediction by Wu *et al.*[21] of a N_2 state that breaks up asymmetrically with a dissociation energy of 53.9 eV and with a barrier height of 1.3 eV. The barrier height is the energy difference between the maximum energy of the barrier of the PEC minus the energy at the dissociation limit. We find that the $2^3\Pi_u$

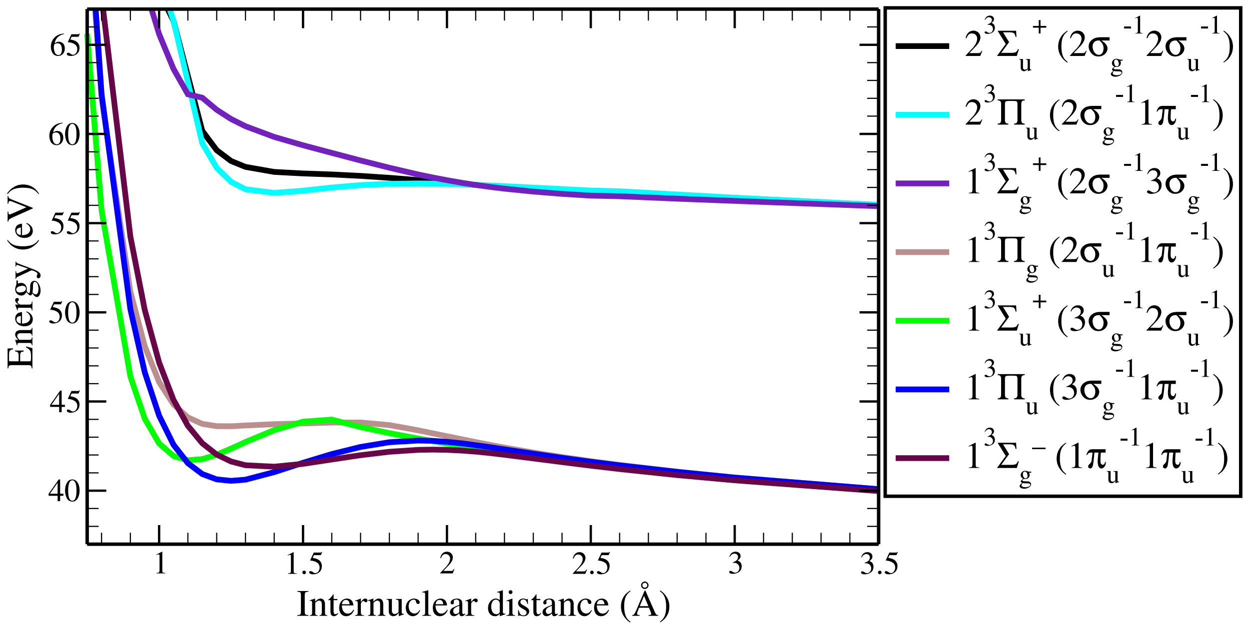

FIG. 6. PECs of triplet doubly ionized states of N_2 with two valence holes.

state has a dissociation energy of 55.8 eV and a barrier height of 1.4 eV. Hence, our results suggest that the state observed experimentally is the $2^3\Pi_u$ state.

Next, to compare our results with previous theoretical work,[21,23,55] we also employ the CASSCF+MRCI method in order to compute the doubly ionized states of N_2 with two outer valence holes. In particular, in Table III we show our results and the results of previous work for the vertical, adiabatic and dissociation energies of these states. We find that our results for states A in Table III, which correspond to N_2 states with two outer valence holes, are in excellent agreement with the values obtained in previous theoretical work.[21,55] In addition, the calculated VIE is in good agreement with previous experimental findings.[32] For completeness, we also show in Table III our results for N_2 states with at least one inner valence hole, denoted by states B. We find that the vertical ionization energies of the states $5^1\Sigma_g^+$ and $2^1\Sigma_u^+$ are in reasonable agreement with previous experimental results.[32]

2. *Core states*

We now compute the PECs for the doubly ionized states of N_2 with one or two core holes in the large core-valence augmented quintuple zeta (aug-cc-pCV5Z) basis set.[54] Previous theoretical studies[56,57] have only addressed the energy of N_2 states with two core holes at equilibrium distance

TABLE III. Doubly ionized states of N_2 with two valence hole. DE is computed at an internuclear distance of 4 Å. All energies are expressed in eV.

States	main electronic	Present calculations (CASSCF+MRCI)			Previous work		Exp.[c]
A	configuration	VIE	AIE	DE	VIE	AIE	VIE
$1^1\Sigma_g^+$	$3\sigma_g^{-2}$	42.70	42.68	42.16	42.5[a]	42.6[b]	43.4
$1^1\Delta_g$	$1\pi_u^{-2}$	46.72	44.21	42.20	46.5[a]	44.09[b]	46.7
$1^1\Pi_u$	$1\pi_u^{-1}$,$3\sigma_g^{-1}$	45.12	44.19	42.25	44.9[a]	44.11[b]	44.7
$1^1\Sigma_u^+$	$2\sigma_u^{-1}$,$3\sigma_g^{-1}$	50.57	50.53	46.06	50.4[a]	-	50.3
$1^1\Pi_g$	$1\pi_u^{-1}$,$2\sigma_u^{-1}$	49.12	-	42.26	49.0[a]	-	48.9
$1^3\Sigma_g^-$	$1\pi_u^{-1}$,$1\pi_u^{-1}$	45.69	43.55	42.20	45.5[a]	43.41[b]	-
$1^3\Pi_u$	$1\pi_u^{-1}$,$3\sigma_g^{-1}$	43.59	42.76	42.25	43.4[a]	42.69[b]	-
$1^3\Sigma_u^+$	$2\sigma_u^{-1}$,$3\sigma_g^{-1}$	44.11	44.11	42.18	43.9[a]	44.10[b]	45.0
$1^3\Pi_g$	$1\pi_u^{-1}$,$2\sigma_u^{-1}$	46.42	46.08	42.27	46.3[a]	46.06[b]	-
		Present calculations (CASSCF)				-	
$2^1\Sigma_g^+$	$1\pi_u^{-2}$	44.99	42.38	39.46	46.5[a]	44.65[b]	46.8
$3^1\Sigma_g^+$	$2\sigma_u^{-2}$	56.54	-	43.73	-	-	57.4
States	main electronic	Present calculations (CASSCF)			Previous work		Exp.[c]
B	configuration	VIE	AIE	DE	VIE	AIE	VIE
$4^1\Sigma_g^+$	$2\sigma_g^{-1}$,$3\sigma_g^{-1}$	61.55	56.49	57.24	-	-	67.4
$5^1\Sigma_g^+$	$2\sigma_g^{-2}$	92.33	-	68.28	-	-	94.8
$2^1\Pi_u$	$1\pi_u^{-1}$,$2\sigma_g^{-1}$	68.08	61.20	59.91	-	-	-
$2^1\Sigma_u^+$	$2\sigma_u^{-1}$,$2\sigma_g^{-1}$	67.92	64.97	59.90	-	-	70.8
$1^3\Sigma_g^+$	$2\sigma_g^{-1}$,$3\sigma_g^{-1}$	62.22	-	55.73	-	-	-
$2^3\Pi_u$	$1\pi_u^{-1}$,$2\sigma_g^{-1}$	62.91	56.69	55.77	-	-	-
$2^3\Sigma_u^+$	$2\sigma_u^{-1}$,$2\sigma_g^{-1}$	63.25	-	55.56	-	-	-

[a] Ref. 55

[b] Ref. 21

[c] Ref. 32

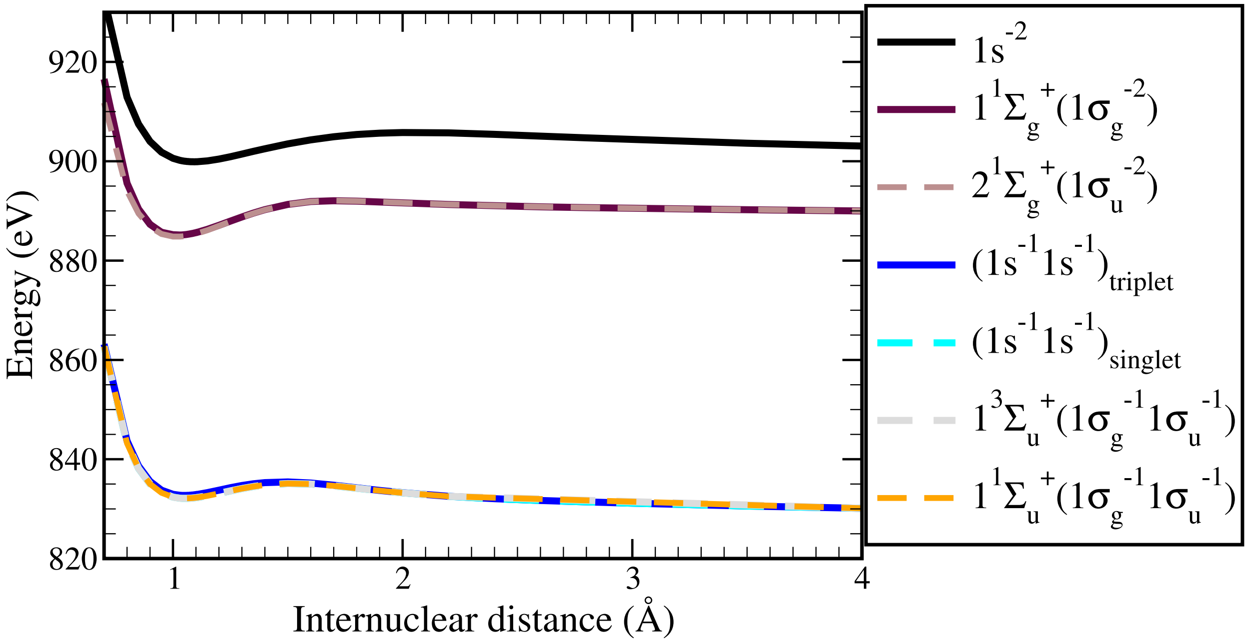

FIG. 7. PECs for the doubly ionized states of N_2 with two core holes. The state $1s^{-2}$ refers to the removal of two electrons from the same site of localized orbital 1s. The state ($1s^{-1}$ $1s^{-1}$) refers to two electrons being removed from localized 1s orbital from different sites.

of the ground state of N_2. Hence, to the best of our knowledge, the PECs shown in Figure 7 and Figure 8 have not been previously reported. To compute the PECs for N_2 states with one or two core holes we use the two-step optimization process within the framework of CASSCF, which we also employed to compute the PECs of doubly ionized N_2 states with a core hole. Namely, first, we freeze the orbital(s) with holes while simultaneously restricting its (their) occupancy. Next, we optimize the previously frozen orbitals while freezing all the remaining active occupied orbitals.

As for the singly ionized states of N_2 states with one core hole, we compute the PECs of N_2 states with two core holes using both localized and delocalized core orbitals. Figure 7 shows the calculated doubly ionized states of N_2 with two core holes with respect to the ground state energy of N_2. As expected, we find that the PECs for $1s^{-2}$, $1^1\Sigma_g^+$ and $2^1\Sigma_g^+$ states, which correspond to two electrons missing from the same orbital, are higher in energy than the PECs of all other states where electrons are missing from different orbitals. Figure 8 shows the PECs for the singlet and triplet states of N_2 with one core and one valence electron missing. Comparing Figures 8(a) with 8(b) we find that the states with one core and one inner valence hole have the same DE for the singlet and triplet spin symmetries. Moreover, we find that a common feature among the PECs of doubly ionized states of N_2 with one or two core holes is the existence of an energy minimum and

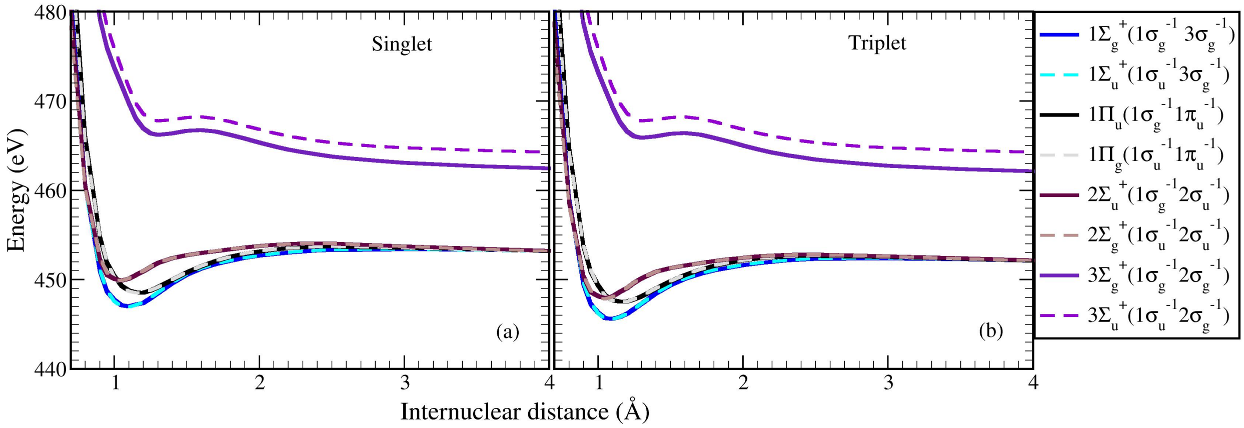

FIG. 8. PECs for the doubly ionized states of N_2 with a single core hole and a valence hole.

a maximum, i.e. barrier, for increasing internuclear distance.

Previous work[56] on the double core hole states of N_2 reported an ionization energy of 901.1, 835.8 and 836.4 eV for the $1s^{-2}$, $1s^{-1}1s^{-1}$ singlet and triplet states, respectively, using localized orbitals. In this work, we obtain vertical ionization energies at 1.10 Å, of 899.9, 832.8 and 832.3 eV for the corresponding states using localized orbitals. The small difference between our results and those reported previously[56] can be attributed to the different basis sets employed. Specifically, we employ an aug-cc-pCV5Z basis set while a less accurate cc-pVTZ basis set is employed in Ref. 56. For states with two core holes in the $1\sigma_g$ and $1\sigma_u$ orbitals we find the vertical ionization energy to be equal to 885.6 and 885.4 eV respectively. These values are in agreement with the measured ionization energy of 902.55 eV reported in Ref. 57.

IV. CONCLUSIONS

We have presented the potential energy curves for all singly and doubly ionized states of N_2. To our knowledge, PECs for doubly ionized states of N_2 with at least one inner valence or a core hole, have not been previously reported. To obtain the PECs for singly or doubly ionized states of N_2 with outer valence holes, we employ the CASSCF method and optimize in a single step all ten active orbitals of N_2. On the other hand, to obtain the PECs for singly ionized N_2 states with a core hole as well as for doubly ionized states with at least one inner valence or core hole, we employ a two-step optimization process within the framework of CASSCF. That is, in the first step we freeze the orbitals with holes, restrict their occupancy, and optimize the remaining active orbitals. In the second step, we optimize the orbitals with holes and freeze the rest of the active orbitals that have been optimized in the first step. We repeat this process until convergence is achieved. This two-step optimization process have been previously employed in the context of singly ionized states of N_2 with a single core hole.[25–27] Hence, in this work we have demonstrated the general applicability of this technique to the doubly ionized states of N_2. Moreover, we have demonstrated very good agreement with previously reported calculations and/or experimental results. The potential energy curves presented here will serve as a reference for explicitly accounting for nuclear motion during the interaction of free electron laser pulses interacting with diatomic molecules, such as N_2.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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