The impact of vibrational wave function on low energy electron vibrational scattering from nitrogen molecule*

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The vibrational wave function of the target theoretically plays an important role in the calculation of vibrational excitation cross sections. By a careful study of the differential cross sections resulting from different vibrational wave functions we find that cross sections are susceptible to vibrational wave functions. Minor changes in the vibration wave function may cause a significant change in the cross section. Even more surprising is that by selecting a few numbers of potential models (which determine the vibrational wave functions) we can often calculate the differential scattering cross section in much closer agreement with experiment in the framework of body-frame vibrational close-coupling theory, which suggest that an accurate potential energy may play a more important role in scattering than we thought before.

Keywords: vibrational scattering, vibrational wavefunction, nitrogen molecule

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1. Introduction

The collision of electrons is widely used in many areas such as physics, chemistry, astrophysics, and even biology.[1–3] One of the most difficult parts of the electron collision lies in low energy scattering where quantum detail of the incident electron and target is very important. In low energy electron–molecule scattering ($E < 10$ eV), the core processes are elastic scattering and ro-vibrational excitation. An accurate approach to deal with this problem is the body-frame vibrational close-coupling (BFVCC),[4–6] in which the total wave function is expanded in terms of the rotational, vibrational and electronic states of the target. Under this framework, if the expansion of wave function is completely strict, one will get the exact physical description of the scattering process. However, many approximations have to be introduced to find a balance between theoretical strict and practical program implementation, such as the rotational motion is treated adiabatically (and can be averaged), electronic states are confined to the ground state for the energy exchange is small, many-body correlation and induced polarization effects are modeled by potentials (better than adiabatic (BTAD),[7] distributed spherical Gaussian (DSG).[8]) After this hard work, BFVCC studies have provided many good agreements with the experiment for diatomic systems like N_2,[5,8–10] which is an accepted test molecule in study of accurate electron–molecule interactions[11] and has many important applications in gas lasers, plasmas, and atmospheric physics.[12]

In our previous studies,[9] we find that improving the accuracy of ground state wave function (to obtain better model potentials) to even the convergence results with diffuse orbital cannot offer much help in improving the accuracy of differential cross sections (DCS) of N_2 in the resonance region. We previously thought that one may handle this problem by relaxing the restrictions of ground state (using multiple slater determinants) and introduce more reasonable local potential (energy dependent) to describe polarization effects.[9] However, after a detailed study of the approximation of BFVCC program, it turns out that a small change in vibrational wave function may lead to significant DCS difference. One can often calculate DCS in much closer agreement with experiment by adjusting vibrational wave function even in the resonance region.

The main goal of this study is to investigate the impact of vibration wave function on the vibrational scattering and illustrate that atomic vibration may play a more important role in scattering than we thought before. In Section 2, we provide a brief description of the BFVCC equations and the numerical method to obtain vibrational wave function with certain potentials. In Section 3, we select several potentials (Morse,[5] Hartree–Fock,[13] CCSD(T),[14] and Full CI[14] calculated by GAMESS[15]) and calculate their corresponding vibrational wave functions and DCS. Then, we do several numerical analyses to show that, first, the difference of the low vibrational wave function introduced by similar different model potential is small; second, the small difference leads to obvious changes in DCS calculation; third, one of the four potentials can pro-

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vide much better DCS calculation even in the resonance region according to different scattering situation. We also provide detailed discussion of the reasons for these phenomena. In Section 4, we summarize our work.

2. Theoretical methods

2.1. Scattering equation

For the scattering of low energy electrons and light molecules, one can ignore relativistic effects, the time free Hamiltonian of the scattering system is[16]

$$\hat{H} = \hat{T}_{\rm e} + \hat{H}_{\rm m}^{(\rm e)} + \hat{T}^{(\rm n)} + V_{\rm nn} + V_{\rm coul}, \tag{1}$$

where $\hat{T}_{\rm e}$ is the kinetic term of incident electron, $\hat{H}_{\rm m}^{(\rm e)}, \hat{T}^{(\rm n)}, V_{\rm nn}$ are components of the Hamiltonian of target molecular, and $V_{\rm coul}$ is the Coulomb interaction between incident electron and target molecule. The time-free electron-molecule Schrödinger equation for scattering is

$$(\hat{H} - E)\left|k_0, \alpha_0 v_0 + \right\rangle = 0, \tag{2}$$

where $\left|k_0, \alpha_0 v_0 + \right\rangle$ stand for scattering state.[17] In implementation of BFVCC method[4] to solve Eq. (2), the target molecule is limited in the ground state, and the vibrational dynamics of the target are treated by expanding the system wave function in vibrational states while rotational effects are treated adiabatically and averaged over different molecular orientations. Then, quantum scattering problem equation (2) is in form of coupled integro-differential equations for the radial scattering functions[5]

$$\left[\frac{{\rm d}^2}{{\rm d}r^2} - \frac{\ell(\ell+1)}{r^2} + k_\upsilon^2\right] u^{\Lambda}_{\upsilon\ell,\upsilon_0\ell_0} = 2\sum_{\upsilon'\ell'}\left[V^{\Lambda}_{\upsilon\ell,\upsilon'\ell'}(r)u^{\Lambda}_{\upsilon'\ell',\upsilon_0\ell_0} - \int \mathscr{K}^{\Lambda}_{\upsilon,\upsilon'}(\ell,\ell'|r,r')u^{\Lambda}_{\upsilon'\ell',\upsilon_0\ell_0}(r'){\rm d}r'\right], \tag{3}$$

where subscript 0 means initial state, $u^{\Lambda}_{\upsilon\ell,\upsilon_0\ell_0}$ is the radial coupled scattering function, k_υ^2 is the exit-channel energy, $V^{\Lambda}_{\upsilon\ell,\upsilon'\ell'} = \langle\upsilon,\ell;\Lambda|V^{\rm scp}|\upsilon',\ell';\Lambda\rangle$ are coupling matrix elements of the static and correlation/polarization local potentials, and $\mathscr{K}^{\Lambda}_{\upsilon,\upsilon'} = \langle\upsilon,\ell;\Lambda|\mathscr{K}(\boldsymbol{r},\boldsymbol{r}';R)|\upsilon',\ell';\Lambda\rangle$ are the exchange kernel matrix elements of the non-local exchange potential. The polarization potential can be treated by distributed spherical Gaussian (DSG)[8] model or better than adiabatic (BTAD) mode.[7] We compared carefully the two models and found that DSG model is better for e–N_2 system.[9] When BFVCC scattering equation (3) is solved, one gains the scattering functions $u^{\Lambda}_{\upsilon'\ell',\upsilon_0\ell_0}$. Then the scattering matrix T can be calculated[17] which finally gives the differential cross section.[9]

2.2. The role of vibrational wave function

The importance of vibrational wave function is reflected with construction of vibrational coupling potentials (V and $\mathscr{K}$ in Eq. (3)) by integrating product of the interaction potential and pairs of vibrational wave functions over the internuclear distance R.[4] The local term V considers static and correlation/polarization effect:

$$V^{\rm scp}(r) = V^{\rm st}(r) + V^{\rm cp}(r) = \sum_0^\infty \upsilon_\lambda^{\rm scp} P_\lambda(\cos\theta) \tag{4}$$

and $\lambda = 14$ is required to obtain a numerical converged result for the e–N_2 system. For the static interaction (radical part), the integration over R is required to evaluate the vibrational coupling potentials:

$$\begin{aligned}\omega^{\lambda}_{\upsilon,\upsilon'}(r) &\equiv \left\langle\varphi_\upsilon^{(v)}\middle|\upsilon_\lambda^{(\rm scp)}\middle|\varphi_\upsilon^{(v')}\right\rangle \\ &= \int_0^\infty \varphi_\upsilon^{(v)*}(R)\upsilon_\lambda^{(\rm scp)}(r,R)\varphi_{\upsilon'}^{(v)}(R){\rm d}R.\end{aligned} \tag{5}$$

Introduce angular coefficients $g_\lambda(\ell,\ell';\Lambda)$[18] to separate the angle-related part from the radial part,

$$g_\lambda(\ell,\ell';\Lambda) = \left(\frac{2\ell'+1}{2\ell+1}\right)^{1/2} C(\ell'\lambda\ell;\Lambda\,0\,0)C(\ell'\lambda\ell;0\,0\,0), \tag{6}$$

where C is the Clebsh–Gordan coefficient[19] and using the property of the spherical harmonic function and the Clebsch–Gordon coefficient, the matrix element of the local potential energy in Eq. (3) under the base vector representation is

$$V^{\Lambda}_{\upsilon\ell,\upsilon'\ell'}(r) = \sum_0^{\lambda_{\max}} g_\lambda(\ell,\ell';\Lambda)\omega^{\lambda}_{\upsilon,\upsilon'}(r). \tag{7}$$

The non-local exchange-potential comes from anti-symmetry requirement of the wave function of the scattering system. Its kernel is[10]

$$\mathscr{K}(\boldsymbol{r},\boldsymbol{r}';R) = -\sum_{i=1}^{N_{\rm occ}} \xi_i^{\Lambda_i}(\boldsymbol{r};R)\frac{1}{\boldsymbol{r}-\boldsymbol{r}'}\xi^{\Lambda_i^*}(\boldsymbol{r}';R), \tag{8}$$

where ξ is molecular orbital. To calculate exchange-potential matrix in Eq. (3), expand molecular orbital by the spherical harmonic function and deal the electron repulsive potential with multipole expansion. The matrix elements are

$$\mathscr{K}^{\Lambda}_{\upsilon,\upsilon'} = \langle\upsilon,\ell;\Lambda|\mathscr{K}(\boldsymbol{r},\boldsymbol{r}';R)|\upsilon',\ell';\Lambda\rangle. \tag{9}$$

The detailed form of Eq. (9) is complex and can be found in Ref. [10]. The initial and final vibrational wave functions sandwich the exchange kernel and integrated over the internuclear separation R. It is worth mentioning that the exchange potential makes scattering problem become integro-differential equations which is very complicated and time consuming to solve.

2.3. Numerical method for vibrational wave function

The one-dimensional radial Schrödinger equation for vibrational wave functions is solved by the standard Numerov method where the numerical Schrödinger equation can be expressed as[20]

$$\psi_{n+1} \approx \frac{2\psi_n - \psi_{n-1} + 5G_n\psi_n s^2/6 + G_{n-1}\psi_{n-1}s^2/12}{1 - G_{n+1}s^2/12}, \quad (10)$$

in which $G_n \equiv G(x_n) \equiv m\hbar[2V(x_n) - 2E]$, and V used here is obtained by three quantum models (Hartree–Fock (PVQZ), CCSD(T) (PVQZ), and Full CI (PVDZ)) calculated by GAMESS and a fitted Morse[5] model. The energy is scanned from zero to potential upper limit to find the first n eigen-energies and the corresponding vibrational functions. If the scanning energy is exactly the eigenvalue, the classically forbidden condition can be satisfied. To enhance the accuracy, the nodes of each eigen-function and energy mesh reconstruction are taken into account in our numerical approach. If there are n nodes in the wave function, the vibrational quantum number is n for that state.

3. Results and discussion

3.1. Potential models and their wave functions

The four models are used to construct the potential energy curve of N_2 in the ground electronic state. They are illustrated in Fig. 1, from which one can tell that all models catch the main features of diatomic molecules potential: equilibrium position, repulsive interaction within the equilibrium position while attractive interaction without the equilibrium position, and smooth dissociation region. The four models are similar near the equilibrium position but have a relatively large difference near the dissociation region. The purpose of the Full CI and CCSD(T) methods is to describe electron correlation the HF missed. The three models are similar near the equilibrium position while the difference increases with the increase of internuclear distance, which means the electron correlation becomes more and more important when the target molecular atoms away from each other. It is worth noting that HF and CCSD(T) potentials have wrong dissociation behavior: HF increases steadily and CCSD(T) goes up and down respectively. In real quantum calculations, the electron states of molecular are built up by atomic orbital, so when the two atoms separate from each other far away, the very high exited electron atomic orbital and their correlation must be considered, which means the Full CI method has to be introduced. However, the Full CI is very expensive when there are many electrons. In other words, the Full CI method forces us to use relatively small basis sets (PVDZ basis sets are used in our study) which may cause an accuracy decrease in all region potential calculations. In fact, it is still very difficult to obtain the high vibrational excited states (near the dissociation region) either by experiment or theoretical calculation.[21–24] In previous studies of low energy scattering, the system is not likely to be excited to very high vibrational state, only low vibrational exciting (near the equilibrium position) is important, and the dissociation region has relatively small influence on them, so one could just ignore the dissociation region and select one of these similar computations of vibrational wave functions, then much attention is focused on the electron part of the scattering process. However, in the following discussions, one will find, based on these small changes in low vibrational wave functions, the DCS has a significant change.

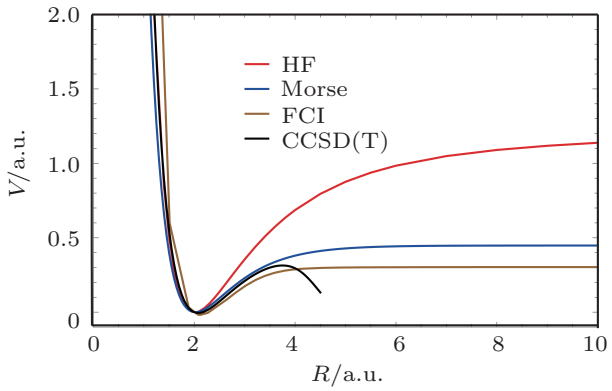


Fig. 1. (color online) The four potential energy curves for N_2 in the ground electron state.

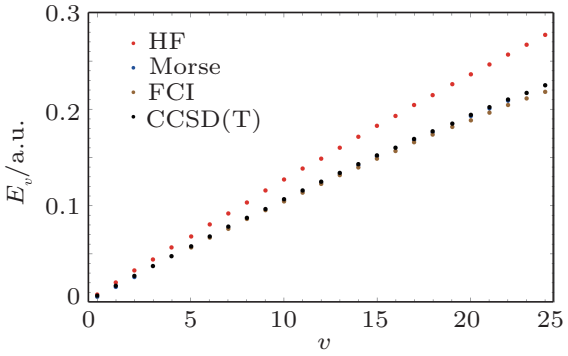


Fig. 2. (color online) The vibrational energy levels for the four potential energy curves. Note that the results of CCSD(T) and Morse are very close to each other.

In our actual calculations, 25 vibrational states are large enough to expand the vibrational part of the scattering wave function (calculation converges). The first 25 vibrational levels we chosen are compared in Fig. 2. One can see that they all go up steadily, which means when incident energy is low, the lower ones are more likely to be involved. The first and last two vibrational wave functions we chose are illustrated in Figs. 3(a)–3(d). One can note that the wave functions are similar to each other, they all share the same wave form, however the similarity goes down with the vibrational level and the interatomic distance R. In the potential side, from Fig. 1 one can see that the similarity goes down with R as well. It is worth noting that, the potential is very similar with each other

(except the HF model) in $R < 3.5$ a.u., while the highest vibrational state we choose is in $R < 3.2$ a.u. (most part is within 3) and shows a clear difference. That is because the quantum effect produces wave function based on the whole potential curve (up to the upper limit, see Subsection 2.3) even if you only need the low local state. The dissociation region affects the vibrational states we used, and may be important in the low energy scattering.

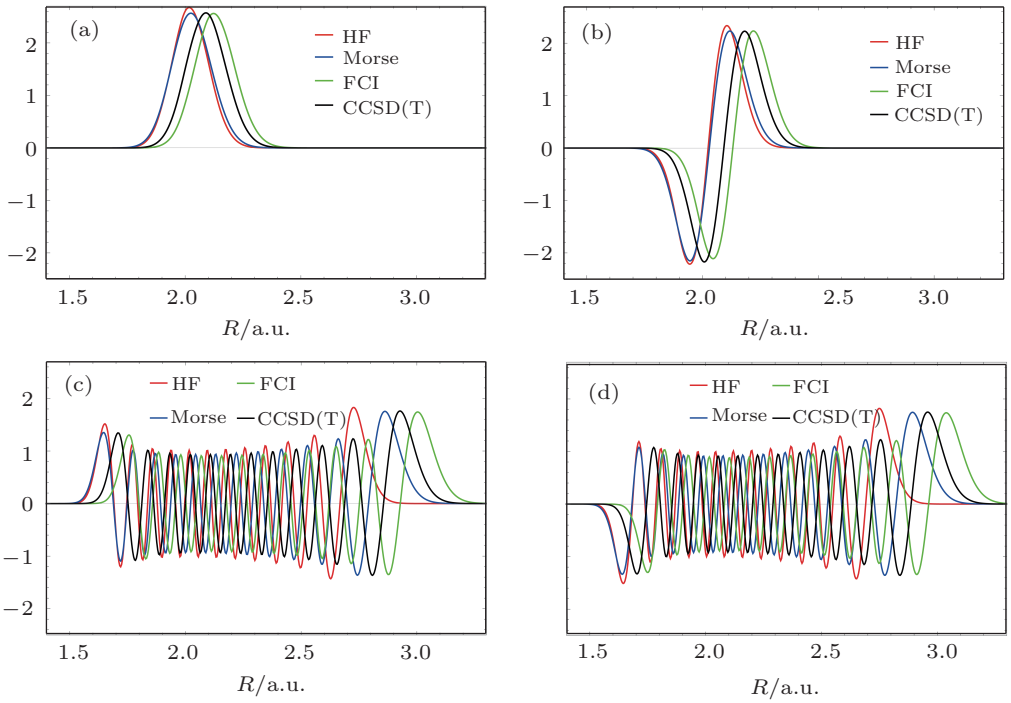


Fig. 3. (color online) The vibrational wave functions for the four potential energy curves: (a) $v = 0$, (b) $v = 1$, (c) $v = 23$, and (d) $v = 24$.

3.2. Best potential energy curve for DCS calculation with different incident energies

We systematically calculated the DCS by increasing the incident energy to test the four sets of vibrational wave functions. The results are shown in Figs. 4–8. It appears that, when energy is low (Figs. 4 and 5) the HF and Morse models fit the experiment best. When energy is high (Fig. 8), the CCSD(T) and FCI models fit the experiment best. In the resonance region (Fig. 7), the HF and FCI models work better than other models. The reason for this is that, when the incident energy is low, the molecular system is hard to excite to high vibrational states, the lower vibrational wave functions are more important. The HF and Morse potentials are more accurate in these regions because in HF we can choose a very large base set to calculate accurate potential and in Morse the potential is fitted by the experimental results which are accurate in low vibrational levels. In FCI model the base set is relatively small, so the results may not be as accurate as HF and Morse. Because the wave functions are determined by the whole potential, the above discussion is qualitative. However, from Figs. 3(a) and 3(b) one can see that the Morse and HF models are indeed very similar to each other in low vibrational states. When the incident energy is high, the high vibrational states become important, the FCI and CCSD(T) methods become more accurate than the two others, which means they give a relatively better dissociation behavior than the HF and Morse potentials.

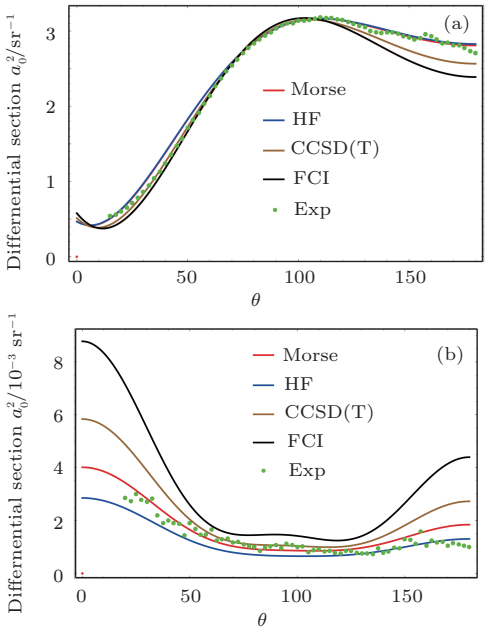


Fig. 4. (color online) Elastic differential cross sections for e–N_2 scattering at $E = 0.80$ eV for panels (a) 0–0 and (b) 0–1. Experiment data are taken from Ref. [25].

It is more complicated in the resonance region, in 0–0 scattering (Fig. 7(a)), the HF model is the best, while in 0–1 scattering (Fig. 7(b)) the FCI catches up. The laws behind are the same, the 0–1 scattering involves excited states explicitly

which means the energy exchange is larger and high vibrational states are more important.

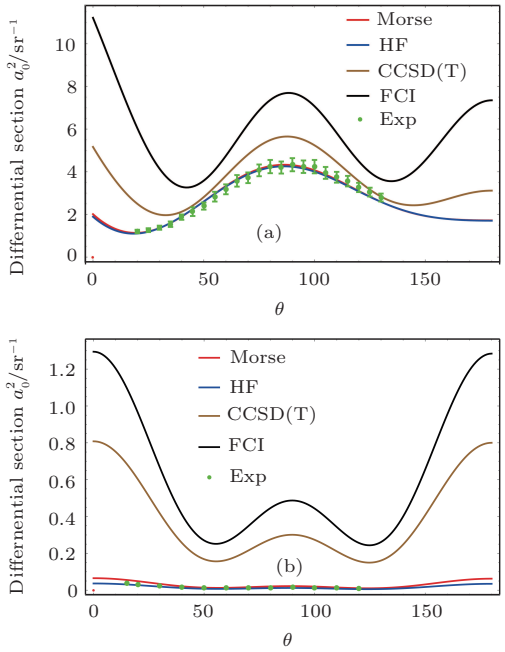


Fig. 5. (color online) Elastic differential cross sections for e–N_2 scattering at $E = 1.50$ eV for panels (a) 0–0 and (b) 0–1. The experiment data are taken from Ref. [5] for panel (a) and Ref. [26] for panel (b).

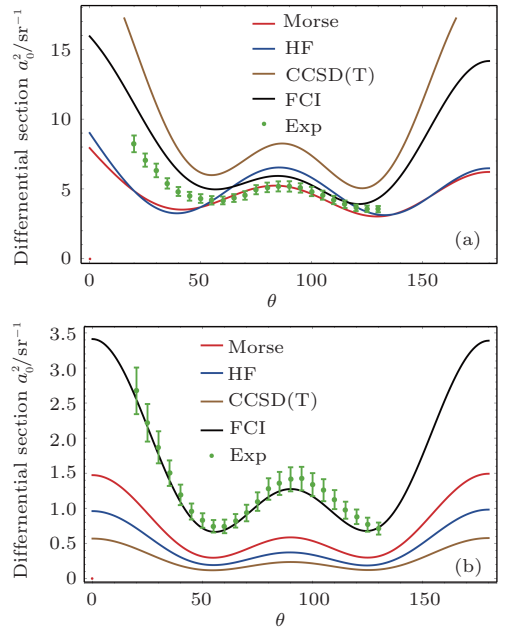


Fig. 6. (color online) Elastic differential cross sections for e–N_2 scattering at $E = 1.98$ eV for panels (a) 0–0 and (b) 0–1. The experiment data are taken from Ref. [5].

However, in the resonance region, the interaction time is relatively long, vibrational states are relatively more involved, so the requirement for a whole accurate vibrational wave functions and hence the whole region potential energy curve are needed (many-body correlation effect must be considered, like FCI). Finally, it is worth noting that, in the four models, there is always a potential fitting the experiment well, which means that the vibrational part of the scattering has been underestimated in comparison with the electron part. A whole region accurate potential is needed to do the right calculation, which is a challenge because accurate potential near the dissociation region is very hard to obtain.

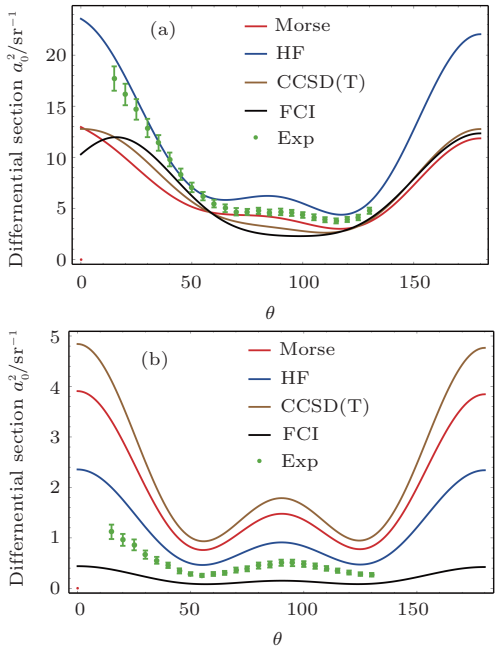


Fig. 7. (color online) Elastic differential cross sections for e–N_2 scattering at $E = 2.46$ eV for panels (a) 0–0 and (b) 0–1. The experiment data are taken from Ref. [5].

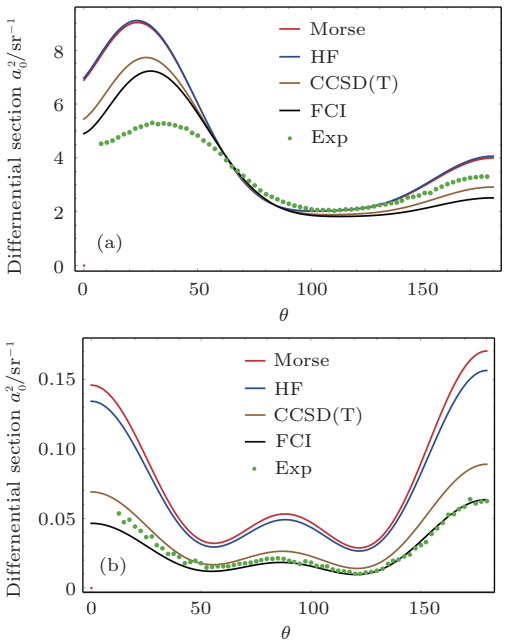


Fig. 8. (color online) Elastic differential cross sections for e–N_2 scattering at $E = 5.00$ eV for panels (a) 0–0 and (b) 0–1. The experiment data are taken from Ref. [25].

4. Conclusion

The low energy electron scattering wave function is expanded by the vibrational states and the electronic states. The electronic part is more complicated and has attracted most of the scientists' attention in previous studies. After a systematically detailed study of the vibrational part by fixing the other

factors affecting the DCS, we find that a small change in the vibrational wave function will cause a significant change in the DCS calculation. Wave functions are determined by potentials. However, it is still very hard for us to obtain accurate potential in the whole region especially near the dissociation region either by experiment or quantum theory calculation. Unfortunately, the potential in the dissociation region can cause a change in vibrational wave function, although the change is small in the low vibrational level, the ultimate impact on the DCS calculation is significant. We compared four usually used potential models and find that no one is perfect for low energy scattering, the HF and Morse methods are suitable for low incident energy, and FCI and CCSD(T) methods are suitable for high incident energy. In the resonance region, all models have an accurate decrease. The HF method is better in 0–0 scattering while the FCI catches up in 0–1 scattering. Generally speaking, the HF potential works well in low incident energy and lowly excited scattering situation while the FCI method works well in high incident energy and highly excited scattering situation. In the resonance region, both models work good but have room to improve. The vibrational part is very important in the low energy scattering and it is still worth finding an accurate one in all the regions including the dissociation part to improve the DCS calculation.

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