

Quantum test of quasiclassical calculations on atom–triatom collisions

D. C. Clary

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Fermi-Amaldi theory which apparently cause the direct subtraction of the total binding energies, $I.P. = E_{N-1} - E_N$, to produce negative ionization potentials (see Table I).

The implementation of the method described above is straightforward and Table I shows the results for a few atoms and ions in comparison with experiment,¹⁰ Thomas-Fermi results in the Sommerfeld approximation,^{8,3} Thomas-Fermi-Amaldi results,⁵ and two calculations simplified by use of Latter's⁹ analytical approximation to the Thomas-Fermi potential, with and without the Fermi-Amaldi correction [i.e., Eqs. (6) and (5) in Ref. 9]. However, since the Latter potential is a neutral atom potential, it must be modified to be used in the above scheme. The potential was modified via the relation ($Z = N$)

$$V_{N-a}(r) = -\frac{Z}{r} + \frac{(N-a)}{N} \lambda \left(\frac{Z}{r} + \phi(r) \right), \quad (8)$$

where a is the number of electrons removed from the neutral atom, $\phi(r)$ is Latter's potential and λ is either one or the Fermi-Amaldi correction factor [namely, $(N-a-1)/(N-a)$]. This means that the electron repulsion part of the Latter potential is scaled down in relation to the number of electrons present.

In order to understand the results in Table I one must realize that none of the computational methods allows for spin polarization or shell structure. Thus they cannot be expected to reproduce the detailed variation in the experimental ionization potential as a function of Z . The

best one can hope for is a monotone decrease as based on the ionization potentials of the noble gas elements. Such a trend is indeed shown by the TF, TFA, and TFA-IK results but not by the calculations based on the Latter potential. However, the magnitudes are poorly reproduced by the TF, TFA, and L-IK and, to a lesser extent, by the LFA-IK theory. The magnitudes obtained by the TFA-IK method here proposed are a bit low but not unreasonable given the character of the theory.

We conclude that, while error variation between the neutral and ion calculation of total binding energy causes negative ionization potentials to be obtained from the Thomas-Fermi-Amaldi theory when applied in the usual manner, this problem can be largely eliminated by the use of an inverse Koopmans method as described above.

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Quantum test of quasiclassical calculations on atom-triatom collisions

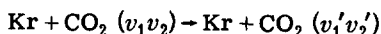
D. C. Clary^{a)}

Department of Chemistry, University of Manchester, Manchester, M13 9PL, United Kingdom

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In this Note, exact quantum calculations are used to examine the accuracy of recent quasiclassical results^{1,2} for the energy transfer in collinear Kr + CO₂ collisions.

Vibrational transition probabilities $P(v_1v_2 \rightarrow v'_1v'_2)$ for the collinear process



have been computed with a quantum-dynamical method which is described in detail in Ref. 3. v_1 and v_2 are the quantum numbers of the symmetric stretch and asymmetric stretch vibrational modes of CO₂, respectively. The potential energy surface used here and in the quasiclassical calculations^{1,2} is due to Suzukawa *et al.*⁴ and is expanded as a sum of a molecular term, V_{CO_2} , and an interaction term, V_{int} . V_{CO_2} is either a harmonic poten-

tial (V_{Har}) or an anharmonic potential⁵ (V_{Anh}) expressed in terms of bond displacements. V_{int} is expanded⁴ as a sum of atom-atom pair potentials, which are Morse functions connected by splines to van der Waals functions.

In the quasiclassical calculations^{1,2} $P(v_1v_2 \rightarrow v'_1v'_2)$ were not computed. Instead, results were reported of the average energy transferred from translation to vibration, $\Delta E(v_1v_2)$, for initial level (v_1v_2). In quantum calculations, this quantity is defined by

$$\Delta E(v_1v_2) = \sum_{v'_1v'_2} [E(v'_1v'_2) - E(v_1v_2)] P(v_1v_2 \rightarrow v'_1v'_2),$$

where $E(v_1v_2)$ is the energy of the (v_1v_2) level. Special care was taken in the quantum calculations to ensure converged results. 64 harmonic basis functions were used

TABLE I. $\Delta E(v_1v_2)$ for collinear Kr-CO₂.

Level (v_1v_2)	CO ₂ Potential	$E_{\text{Trans}}(v_1v_2)$ (eV)	$\Delta E(v_1v_2)$ (Quantum) ^a (eV)	$\Delta E(v_1v_2)$ (Quasiclassical) ^{a,b} (eV)
00	V_{Har}	0.5	0.59(-8)	-0.36(-6)
		1.0	0.25(-4)	0.20(-4)
		2.0	0.26(-2)	0.26(-2)
	V_{Anh}	0.5	0.39(-8)	0.11(-4)
		1.0	0.14(-5)	0.44(-4)
		2.0	0.18(-3)	0.27(-3)
01	V_{Har}	0.5	0.99(-7)	-0.49(-6)
		1.0	0.21(-4)	0.16(-4)
		2.0	0.25(-2)	0.25(-2)
	V_{Anh}	0.5	0.32(-4)	0.49(-4)
		1.0	0.11(-3)	0.16(-3)
		2.0	0.48(-3)	0.55(-3)

^aNumbers in parentheses denote powers of ten by which entries should be multiplied.

^bQuasiclassical results taken from Tables II and III, Ref. 2.

to determine the anharmonic molecular states. The number of molecular basis functions (n_B) and integration steps (n_I) needed in propagating the S matrix were $n_B = 16$ and $n_I = 970$ at the lowest energy, and $n_B = 45$ and $n_I = 295$ at the highest energy considered. Good agreement was obtained with quantum transition probabilities reported previously⁷ for collinear Kr + CO₂ collisions in which the potential $V_{\text{Har}} + V_{\text{int}}$ was used. In the previous study⁷ calculations were only carried out in the low energy range, anharmonicity was not considered and no comparisons with quasiclassical results were made.

In Table I, results of $\Delta E(00)$ and $\Delta E(01)$ are presented. Quantum and quasiclassical results obtained using both V_{Har} and V_{Anh} are compared for the same values of $E_{\text{Trans}}(v_1v_2)$, the relative translational energy with respect to the (v_1v_2) level. The quasiclassical $\Delta E(v_1v_2)$ reported in the Table were obtained² by ensemble averaging the difference of final from initial translational energies.

The agreement between the quantum and quasiclassical results for both $\Delta E(00)$ and $\Delta E(01)$ is poor at $E_{\text{Trans}}(v_1v_2) = 0.5$ eV, good at 1.0 eV and excellent at 2.0 eV when V_{Har} is used. For the calculations with V_{Anh} , the quasiclassical results for $\Delta E(00)$ and $\Delta E(01)$ are seen to have a reasonable accuracy in those cases that the quantum $\Delta E(v_1v_2)$ have magnitudes greater than 0.1×10^{-4} eV. The agreement between the quantum and quasiclassical anharmonic results is seen to be better for $\Delta E(01)$ than $\Delta E(00)$. As expected, the quasiclassical $\Delta E(v_1v_2)$ do improve in accuracy as $E_{\text{Trans}}(v_1v_2)$ is increased. At the highest energy considered, $E_{\text{Trans}}(v_1v_2) = 2.0$ eV, the quasiclassical $\Delta E(00)$ and $\Delta E(01)$ overestimate the exact values by factors of 1.5 and 1.1, respectively, when V_{Anh} is employed. These quasiclassical results are not quite so accurate as those obtained with V_{Har} at this energy.

The quasiclassical calculations incorrectly predict that anharmonicity increases $\Delta E(00)$ at $E_{\text{Trans}}(00) = 0.5$ and 1.0 eV, although at $E_{\text{Trans}}(00) = 2.0$ eV, they do correctly predict that $\Delta E(00)$ is decreased by anharmonicity.

In previous quantum calculations⁶ on Kr-CO₂ using a different form of V_{int} to that employed here, it was found, in agreement with the present quantum results, that $\Delta E(00)$ is decreased by anharmonic terms over the whole energy range considered (total energies up to 2.0 eV). The trends in the comparison of quantum and quasiclassical results for $\Delta E(00)$ found here are similar to those observed in studies on atom-diatom collisions.⁸

The dependence of $\Delta E(01)$ on anharmonicity is obtained correctly in the quasiclassical calculations, being increased at $E_{\text{Trans}}(01) = 0.5$ and 1.0 eV and decreased at $E_{\text{Trans}}(01) = 2.0$ eV. At low energies, $V-V$ processes such as $(01) \rightarrow (20)$ are dominant⁷ while at higher energies $V-T$ processes, in particular $(01) \rightarrow (11)$, are more significant.

At higher energies for which the (11) level is open, the incoming Kr atom essentially cannot distinguish between the harmonic (00) and (01) levels for a given value of $E_{\text{Trans}}(v_1v_2)$. For example, in the quantum calculations with V_{Har} at $E_{\text{Trans}}(v_1v_2) = 2.0$ eV, $P(00 \rightarrow 10) = 0.0156$ and $P(01 \rightarrow 11) = 0.0156$, while in the quasiclassical calculations² using V_{Har} , $\Delta E(00) = \Delta E(01)$ to two significant figures for all chosen values of $E_{\text{Trans}}(v_1v_2)$ between 2.0 and 10.0 eV. In the case of V_{Anh} , this feature is also apparent, although it is not quite so dominant. For example, $P(00 \rightarrow 10) = 0.0011$ and $P(01 \rightarrow 11) = 0.0015$ at $E_{\text{Trans}}(v_1v_2) = 2.0$ eV in the quantum calculations with V_{Anh} , while $\Delta E(00)$ and $\Delta E(01)$ differ by less than 25% in the quasiclassical calculations using V_{Anh} for $E_{\text{Trans}}(v_1v_2)$ above 3.0 eV.

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^aPresent address: Department of Chemistry, UMIST, Manchester, M60 1QD, United Kingdom.

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COMMENTS

Some comments regarding the pressure tensor and contact theorem in a nonhomogeneous electrolyte^{a)}

Douglas Henderson

IBM Research Laboratory, San Jose, California 95193

Lesser Blum

Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

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Recently, Henderson *et al.*^{1,2} obtained the contact value theorem,

$$kT \sum_{\alpha} \rho_{\alpha}(0) = p_b + \epsilon E^2/8\pi, \quad (1)$$

for an electrolyte, consisting of charged hard spheres in a dielectric medium, near a uniformly charged hard wall with no image forces. In Eq. (1), $\rho_{\alpha}(0)$ is the contact value of the density profile, $\rho_{\alpha}(x)$, of species α , p_b is the pressure of the bulk electrolyte, $\epsilon E/4\pi$ is the charge density on the wall, and ϵ is the dielectric constant.

Subsequently, Olivares and McQuarrie³ drew attention to the fact that the differential equation from which Eq. (1) was derived, namely,

$$\frac{dp'}{dx} + \sum_{\alpha} \rho_{\alpha}(x) \frac{dv_{\alpha}}{dx} = 0, \quad (2)$$

where $v_{\alpha}(x)$ is the *direct* interaction of a particle of species α with the wall, *appears* to contradict the well known equation from colloid chemistry,

$$\frac{dp''}{dx} + \sum_{\alpha} q_{\alpha} \rho_{\alpha}(x) \frac{d\psi}{dx} = 0, \quad (3)$$

where q_{α} is the charge of species α and $\psi(x)$ is the mean electrostatic potential. We have placed primes on p in dp/dx in Eqs. (2) and (3) for reasons that will become apparent shortly.

Olivares and McQuarrie show that Eq. (2) follows from the Kirkwood definition of the pressure tensor and conclude that Eq. (2) is correct but that Eq. (3) is in error. On the other hand, Carnie and Chan,⁴ using an alternative definition of the pressure tensor, obtain Eq. (3) and conclude that it is Eq. (2) that is in error. Briefly, Carnie and Chan object to Eq. (2) on the basis that the force due to the wall on an ion given by (2) does

not vanish as the distance from the wall increases. This is irrelevant since the force in question is the direct force on an ion due to the wall. When screening is included, the *total* force vanishes. The purpose of this note is to show that both definitions of the pressure tensor are acceptable and have the same physical consequences.

Following Carnie and Chan, the relation between p' and p'' is

$$\nabla \cdot \mathbf{p}' = \nabla \cdot \mathbf{p}'' + \sum_{\alpha\beta} q_{\alpha} q_{\beta} \rho_{\alpha}(\mathbf{r}) \times \int \rho_{\beta}(\mathbf{r}') \nabla_{\mathbf{r}'} u^c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (4)$$

where $q_{\alpha} q_{\beta} u^c(r)$ is the Coulomb part of the pair potential, $u_{\alpha\beta}(r)$, between particles of species α and β (i.e., the part responsible for the screening). Now

$$\psi(\mathbf{r}) = v^c(\mathbf{r}) + \sum_{\beta} q_{\beta} \int \rho_{\beta}(\mathbf{r}') u^c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (5)$$

where $q_{\alpha} v^c(r)$ is the Coulomb part of the direct interaction of a particle of species α with the wall. The last term in either Eqs. (4) or (5) is responsible for the screening. Comparing Eqs. (4) and (5) with Eqs. (2) and (3) we see that Eqs. (2) and (3) are in fact identical. It is essentially a matter of taste whether the screening term is associated with the pressure term or the integral. The only important point is that the screening be included. Equations (2) and (3) are merely two different definitions of dp/dx and hence of p . These two definitions of p differ in a nonhomogeneous fluid but coincide in a homogeneous fluid, where $p = p_b$, the only meaningful pressure in the problem, because of charge neutrality. In addition, the two definitions yield the same contact value theorem.

To make this latter point, we note that if