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Accuracy of Hartree-Fock wave functions for electron-H_2 scattering calculations

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Recent papers on electron-N_2 scattering by Rumble, Stevens, and Truhlar [J. Phys. B **17**, 3151 (1984)] and Weatherford, Brown, and Temkin [Phys. Rev. A **35**, 4561 (1987)] have suggested that Hartree-Fock (HF) wave functions may not be accurate for calculating potentials for use in studying electron-molecule collisions. A comparison of results for electron-H_2 scattering using both correlated and HF wave functions is presented. It is found that for both elastic and inelastic collisions and for all energies considered (up to 10 eV) the HF wave functions yield results in excellent agreement with those obtained from the more accurate wave functions.

Recent papers[1,2] have questioned the utility of Hartree-Fock (HF) wave functions for calculating scattering cross sections of molecules by electrons. The paper by Rumble, Stevens, and Truhlar[1] uses HF and multiconfiguration self-consistent-field first-order configuration-interaction (MCSCF FOCI) wave functions for e-N_2 scattering in the fixed-nuclei approximation. They consider only the static plus a local exchange potential at two internuclear geometries and find that a correlated target wave function strongly affects resonant channels. They suggest that vibrational excitation cross sections may be affected as well. Weatherford, Brown, and Temkin[2] report similar calculations for e-N_2 scattering (the main differences being that they include exchange exactly and use only a MCSCF target wave function) and report similar effects due to correlation. To test the accuracy of HF wave functions for e-H_2 scattering calculations I have employed two different H_2 wave functions in several scattering theories. In all cases, only the ground electronic target state is considered and we are interested here only in rovibrational transitions from the ground rovibrational state to the lowest few rotational and vibrational states.

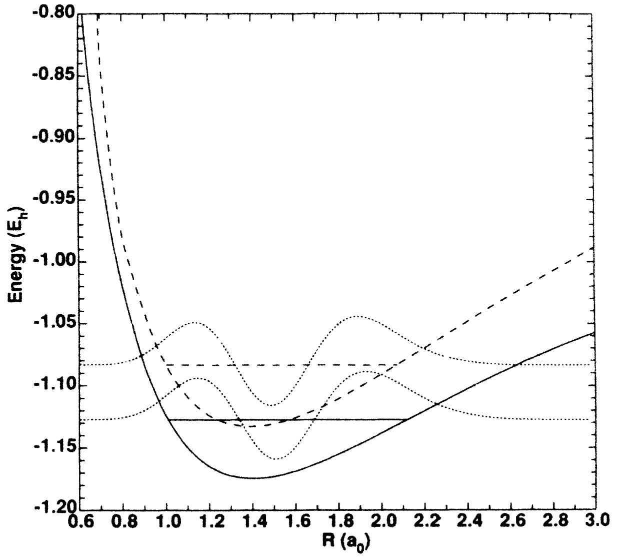

FIG. 1. Electronic energy curves with the $v=2$ vibrational energy level shown. The dashed line was obtained by using the FMA wave functions and the solid line by using the KW wave functions. The $v=2$ vibrational wave functions derived from each curve are shown by the dotted lines. The vibrational wave functions are in arbitrary units and shifted vertically to be centered on their respective vibrational energies.

The HF wave functions used for H_2 are those described by Morrison, Feldt, and Austin[3] (referred to as MFA here). The MFA wave functions were calculated from a $(5s2p/3s2p)$ contracted Gaussian basis using the POLYATOM code (Ref. 4). This wave function is given by a linear combination of appropriately normalized and antisymmetrized products of nucleus-centered molecular orbitals. The form of the orbitals is given by

$$\Phi=\sum_i c_i x^{l_i} y^{m_i} z^{n_i} e^{-\zeta_i r^2} , \tag{1}$$

where the variables subscripted with i are the coefficients determining the basis, and x, y, z, and r [equal to $(x^2+y^2+z^2)^{1/2}$] are the nucleus-centered coordinates.

The correlated wave functions used for comparison are the 54-term H_2 wave functions described in the paper by

TABLE I. Quadrupole moments (ea_0^2).

R (a_0)	MFA	KW
0.5	0.032 98	
0.6		0.099 93
0.8	0.151 10	
1.0	0.243 87	0.257 06
1.2	0.344 66	0.353 56
1.4	0.451 74	0.457 46
1.6	0.564 18	0.564 61
1.8	0.680 51	0.670 99
2.0	0.798 39	
2.2	0.915 91	0.859 85
2.5	1.088 85	
2.6		0.985 75
3.0	1.354 98	

TABLE II. Vibrational energies (E_h).

v	MFA	KW	Experiment[a]
0	0.0104	0.0100	0.0099
1	0.0303	0.0291	0.0288
2	0.0494	0.0470	0.0467

[a] Reference 11.

TABLE III. Vibrational matrix elements of the quadrupole moments (ea_0^2).

		$\langle v \mid Q(R) \mid v_0 \rangle_R$	
v_0	v	MFA	KW
0	0	0.470 46	0.483 77
0	1	0.090 25	0.087 64
0	2	−0.009 03	−0.011 21
1	1	0.522 76	0.535 69
1	2	0.129 98	0.124 02
2	2	0.575 96	0.586 91

Kolos and Wolniewicz[5] (KW). These wave functions use a basis given in elliptic coordinates. The form of this wave function is

$$\Psi=\frac{e^{-\alpha(\xi_1+\xi_2)}}{2\pi}\sum_{i=1}^{54} c_i\rho^{\mu_i}(\xi_1^{r_i}\eta_1^{s_i}\xi_2^{\bar{r}_i}\eta_2^{\bar{s}_i}+\xi_2^{r_i}\eta_2^{s_i}\xi_1^{\bar{r}_i}\eta_1^{\bar{s}_i}) , \tag{2}$$

where

$$\rho=\frac{2r_{12}}{R} , \tag{3}$$

and α, μ, r, s, $\bar{r}$, $\bar{s}$, and c are the powers and coefficients defining the basis, r_{12} is the interelectronic separation, R is the internuclear separation, and ξ and η are the elliptic coordinates of the two electrons. Note that this wave function is *not* determined by performing a configuration-interaction calculation, but *does* have an explicit dependence on the interelectronic distance.[6]

The vibrational wave functions $\phi_v(R)$ are found from the vibrational Schrödinger equation

$$\hat{\mathcal{H}}(R)\phi_v(R)=\varepsilon_v\phi_v(R) , \tag{4}$$

where $\hat{\mathcal{H}}(R)$ is the vibrational Hamiltonian[7]

$$\hat{\mathcal{H}}(R)=\frac{d^2}{dR^2}+V_{nn}(R)+E^e(R) , \tag{5}$$

μ is the reduced mass of the molecule, $V_{nn}(R)$ is the internuclear potential, $E^e(R)$ is the electronic energy of the molecule at internuclear separation R, and ε_v is the vibrational energy of the state with vibrational quantum v. Note that, unless otherwise noted, atomic units are used in this paper so that, for example, energies are in hartrees ($1E_h=2$ Ry). The vibrational wave function is expanded in a basis of simple harmonic oscillator functions $\xi_{v'}(R)$ as

$$\phi_v(R)=\sum_{v'} c_{vv'}\xi_{v'}(R) , \tag{6}$$

and then the matrix $\langle \phi_v \mid \hat{\mathcal{H}}(R) \mid \phi_{\bar{v}} \rangle_R$ is diagonalized. The eigenvalues are ε_v and the eigenvectors are the coefficients $c_{vv'}$. The vibrational wave functions used here were calculated from a basis of size 10.

Before performing scattering calculations, we can compare the target wave functions in terms of their electronic energies, vibrational wave functions, and their permanent quadrupole moments. Figure 1 shows the electronic energy curves and the vibrational wave functions and energy levels for $v=2$ obtained from each target wave function. It is clear that, although the MFA energies lie considerably above the KW energies and lead to incorrect dissociation of H_2, the vibrational wave functions are almost identical. (The agreement in vibrational wave functions is even better for $v=0$ and $v=1$.) Table I lists the permanent quadrupole moments $Q(R)$ (obtained from the long-range behavior of the potentials) and shows that there is less than a 6% difference in the moments at any internuclear separation. Table II lists the vibrational energies for the lowest-three vibrational states and shows that those calculated from the KW wave functions agree with the experimental values to within 1.5%, while those from the MFA wave functions agree within 7%. Finally, Table III shows the vibrational matrix elements of the quadrupole moment $\langle v \mid Q(R) \mid v_0 \rangle_R$, and we see that except for the $v_0=0$ to $v=2$ element, these elements agree within 5%.

The potentials used in the calculations consist of three parts: static, model exchange, and model polarization. The static potential is calculated simply as the matrix element of the Coulomb potential energy in the target wave function.

The model exchange potential used is the tuned-free-electron-gas exchange model[8] with the "ionization potential" tuned to reproduce body-frame, fixed-R, exact-static-exchange (ESE) eigenphase sums in the Σ_u symmetry at 0.04 Ry. Note that this tuning was done *separately* for each target wave function at each internuclear separation. Since the ESE calculations (using the iterative exchange code of Collins *et al.*[9]) were performed for this purpose, they allow a comparison of eigenphase sums which show good agreement over a range of both internuclear separation and energy (see Table IV).

The polarization potential used in all calculations (except the ESE calculations where polarization is not considered) is the variationally determined model potential of Gibson and Morrison,[10] which is based on the MFA wave function and includes nonadiabatic effects via a nonpenetrating approximation.

For a given scattering calculation, the static and exchange potentials and the vibrational wave functions are always determined using *only* the appropriate target wave function. When polarization is considered for the KW target wave function, that part of the potential is the only part not based on the KW wave function. The scattering calculations also require channel energies which, in *all* calculations, were obtained from the experimental rovibrational constants.[11]

In addition to the ESE calculations mentioned above, calculations were performed in the space-fixed reference

TABLE IV. Selected exact-static-exchange eigenphase sums and cross sections.

	Σ_g		Σ_u	
E (Ry)	η (rad)	σ (a_0^2)	η (rad)	σ (a_0^2)
		$R=1.0a_0$		
0.04	2.7634[a]	43.57	0.0251	0.172
	2.7630[b]	43.68	0.0250	0.170
0.09	2.5823	40.00	0.0612	0.479
	2.5818	40.10	0.0601	0.459
0.16	2.4104	35.67	0.1202	1.063
	2.4096	35.75	0.1175	1.011
0.25	2.2500	31.04	0.2004	1.901
	2.2488	31.11	0.1962	1.818
		$R=1.4a_0$		
0.04	2.7248[a]	52.97	0.0488	0.656
	2.7244[b]	53.07	0.0474	0.619
	2.7246[c]	53.03	0.0493	0.676
0.09	2.5265	47.83	0.1227	1.930
	2.5258	47.94	0.1181	1.781
	2.5260	47.90	0.1233	1.940
0.16	2.3399	41.75	0.2460	4.413
	2.3386	41.85	0.2363	4.066
	2.3399	41.82	0.2459	4.387
0.25	2.1678	35.44	0.4091	7.640
	2.1656	35.51	0.3950	7.134
	2.1679	35.48	0.4084	7.583
		$R=1.8a_0$		
0.04	2.6881[a]	62.67	0.0908	2.331
	2.6875[b]	62.78	0.0859	2.076
0.09	2.4737	55.67	0.2523	8.212
	2.4726	55.78	0.2359	7.169
0.16	2.2736	47.54	0.5293	19.336
	2.2715	47.64	0.4959	17.129
0.25	2.0915	39.33	0.8381	27.122
	2.0880	39.41	0.7985	25.146

[a] MFA HF wave-function results.
[b] KW accurate wave-function results.
[c] HF results in Ref. 9.

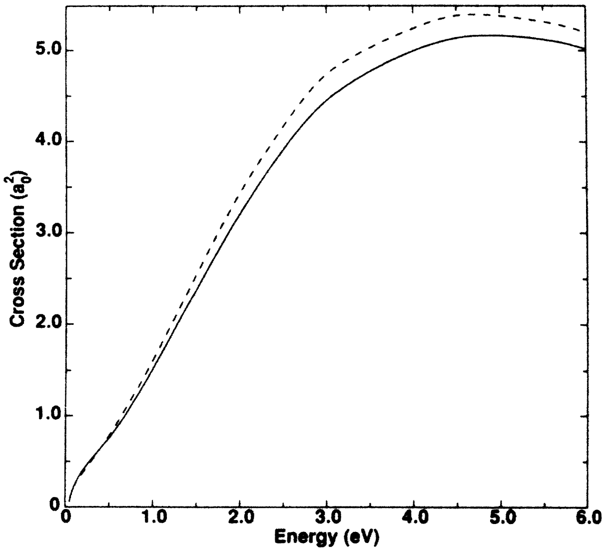

FIG. 2. Rotational excitation cross sections for e-H_2 scattering in the rigid-rotor approximation. The notation is as in Fig. 1.

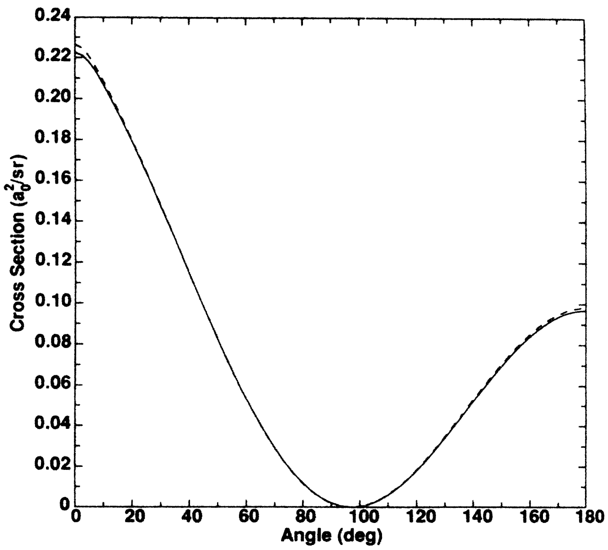

FIG. 3. Differential cross sections for e-H_2 scattering for pure vibrational excitation to the $v=1$ state at 4.5 eV. The notation is as in Fig. 1.

TABLE V. Selected cross sections from full laboratory-frame rovibrational close-coupling calculations using the full static, exchange, and polarization potentials. The results using the KW wave function are listed directly below the MFA wave-function results. All cross sections are in a_0^2 and the energies are in eV.

	$\sigma_{v_0 j_0 \to vj}$					
E (eV)	00→00	00→02	00→10	00→12	00→20	00→22
0.8	48.625	1.6843	0.0906	0.0550		
	49.741	1.7128	0.0923	0.0544		
1.0	50.106	2.2207	0.1790	0.1375		
	51.136	2.2511	0.1824	0.1368		
2.0	53.581	4.8022	0.6916	0.7927	0.0246	0.0456
	54.189	4.8521	0.6895	0.7919	0.0243	0.0441
3.0	52.289	5.9880	0.7812	1.0114	0.0587	0.0887
	52.649	6.0759	0.7777	1.0138	0.0594	0.0865
4.5	47.087	6.1120	0.6186	0.8599	0.0508	0.0635
	47.226	6.2280	0.6162	0.8657	0.0524	0.0633
6.0	41.426	5.5946	0.4504	0.6361	0.0380	0.0426
	41.426	5.7134	0.4472	0.6384	0.0398	0.0437

frame incorporating both rigid-rotor[12] and full rovibrational close-coupling theories.[13,3] Rovibrational close-coupling results using the MFA wave function have been previously published[14] showing the dramatic breakdown of the adiabatic-nuclei formulation[15] of scattering theory for vibrational excitation of H_2. Both integrated and differential cross sections were obtained and all results were converged to at least 1%. Figure 2 compares the integrated rotational excitation cross sections obtained from the two target wave functions in rigid-rotor calculations. Figure 3 compares differential cross sections for vibrational excitation at a scattering energy of 4.5 eV. Table V lists selected integrated cross sections for various rovibrational transitions. As these representative results show, the HF wave-function results are, in all cases, in good agreement with the KW wave-function results.

It appears that accurate scattering calculations may not require explicit treatment of electron correlation in the determination of the target wave function, at least in the case of low-energy e-H_2 scattering. One indication that this might be the case is the agreement of the quadrupole moments, their vibrational matrix elements, and the vibrational wave functions that was seen in Tables I–III in and Fig. 1. However, these do not probe the short-range parts of the scattering potential. H_2 may be an anomalous case, having only two electrons and no pronounced resonance associated with the calculations reported here. Other systems deserve careful study to determine the conditions under which the correlation of the target wave function is important for electron-molecule scattering.

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