Transferability of local-density norm-conserving pseudopotentials to electron-molecule-collision calculations

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We present an application of pseudopotentials to *ab initio* calculations of elastic and electronically inelastic electron-molecule-collision cross sections. We use the Schwinger multichannel method (SMC) implemented with the local-density norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter [Phys. Rev. B **26**, 4199 (1982)]. In our procedure, the core electrons and protons are replaced by the nonlocal but single-particle pseudopotential and the valence electrons are treated in a many-body framework, as in the SMC method. Our calculated integral and differential cross sections are in very good agreement with previous all-electron calculations.

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I. INTRODUCTION

Although collision cross sections of low-energy electrons with many-electron molecules play an important role in plasma and industrial processes, there are few experimental [1] and theoretical [2] results for these systems. If the existing *ab initio* methods are also intended to help experimentalists, molecules having hundreds of electrons must be studied. In recent years, the study of low-energy electron-molecule collisions using the Schwinger multichannel (SMC) method [3–5] has been done successfully for some linear targets and some small polyatomic targets with arbitrary geometry, in elastic and in inelastic scattering [6–11]. However, for polyatomic molecules with heavy atoms, theoretical results are scarce. In the SMC method, the main difficulty in obtaining cross sections for these systems is due primarily to the computational effort in the evaluation of the primitive two-electron integrals

$$\langle\alpha\beta|V|\gamma\mathbf{k}\rangle = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \alpha(\mathbf{r}_1)\beta(\mathbf{r}_1)\frac{1}{r_{12}}\gamma(\mathbf{r}_2)e^{i\mathbf{k}\cdot\mathbf{r}_2} \tag{1}$$

which involve three Cartesian Gaussian functions and a plane wave. These primitives must be evaluated for all possible combinations of α, β, and γ and for several directions and moduli of $\mathbf{k}$. The number of these integrals is very large, consuming a considerable part of the computation time for the entire calculation.

Recently, the SMC method was implemented in distributed-memory parallel computers which permit groups of primitive integrals to be evaluated simultaneously, allowing studies of collisions by molecules formed by heavier atoms. Integral elastic cross sections, momentum-transfer, and differential cross sections for molecules such as SiH_4, GeH_4, and Si_2H_6 were obtained in the static-exchange approximation using these powerful computers [2].

For the low-energy collision processes, only the valence electrons are important, the core electrons becoming an unwanted burden that just increases the computation time. The proper way to eliminate the core electrons is, of course, through the use of pseudopotentials (PP). Aside from the asset of eliminating the core electrons, PP have the advantage of rendering the valence wave functions much smoother; therefore, they can be expanded in much shorter bases. PP allow a great simplification in treating systems with many electrons. For instance, consider molecules such as SiF_4, $SiCl_4$, $SiBr_4$, and SiI_4. After eliminating the core they become equivalent to CF_4 with just 32 valence electrons. The advantage in the computational cost is evident. Without this simplification studies involving these systems are almost impossible. In Table I we show the number of electrons (N_e) and of the Cartesian Gaussian functions (N_{CG}) used in the scattering calculations for some typical molecules in the all-electron (AE) and pseudopotential cases.

Though the PP were first defined by orthogonalization to core states [12], nowadays one prefers the smooth and energy-independent pseudopotentials, the *norm-conserving* pseudopotentials [13–16], which were introduced by Hamann, Schlüter, and Chiang [17]. They are obtained from AE atomic calculations made within the local-density approximation (LDA) and produce valence true wave functions and pseudo-wave-functions that are identical beyond some core radius r_c. No orthogonalization to core states is ever made, in contrast to the Phillips and Kleinman construct. Bachelet, Hamann, and Schlüter (BHS) [18] extended the Hamann-Schlüter-Chiang pseudopotentials to include relativistic effects and tabulated the PP for many atoms of the Periodic Table. They fitted analytical functions (Gaussian and error function) to the numerical PP so that matrix elements

TABLE I. Number of electrons N_e and of Cartesian Gaussian functions N_{CG}.

	N_e		N_{CG}	
Molecule	AE	PP	AE	PP
CH_4	10	8	40	32
CH_2O	16	12	68	52
SiH_4	18	8	72	49
Si_2H_6	34	14	136	84
GeH_4	36	8	93	62

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in a Gaussian or plane-wave basis can be calculated in closed form.

Though they are derived from LDA atomic calculations, the BHS pseudopotentials are assumed to have optimal transferability to different systems, situations, and methods. Transferability cannot be proved, but has to be verified in specific calculations. Within the LDA framework, the transferability has been verified by the many band-structure calculations that are current in the literature. On the other hand, there are not many instances when these norm-conserving PP were used within the Hartree-Fock (HF) framework: we can only quote a HF band calculation [19], calculations on atoms and diatomic molecules [20], and the calculation of scattering of electrons by atoms [21, 22]. Since the HF and LDA frameworks are so different, and because of the importance of the norm-conserving pseudopotentials, we found that the question of transferability to HF calculations should be studied further.

In this paper we present an application of the BHS pseudopotentials in HF molecular-structure calculations and in low-energy electron-molecule scattering calculations. One readily understands why the HF framework, and not the LDA, is being used: the HF approximation (or any methodology based in a combination of Slater determinants) keeps the many-body character of the wave function and allows a description of the valence excited states of a molecular system. Such a description is necessary in the calculations of electronic excitation cross sections by low-energy electron impact. The LDA, being a ground-state and density (not wave-function) description, is unable to treat such a problem. On the other hand, one might ask why not consistently use PP defined in the HF framework instead of the BHS pseudopotentials which are LDA based. We think that LDA affords better ways to define the PP than the HF framework, for instance, by its ability to deal with fractional-occupation-number configurations.

The success of the transferability of pseudopotentials to electron-molecule-collision studies can lead to other very interesting applications such as in valence molecular photoionization processes and in studies of electron scattering against molecules adsorbed on surfaces. For the photoionization processes, the combination of PP with HF techniques can also be very helpful if one desires to calculate valence autoionization cross sections. For such a problem we need continuum wave functions of the ion mixed with bound electronic excited states of the neutral target. The many-body character of the wave function is again needed, requiring a HF based methodology. The use of electron electronic-energy-loss spectroscopy to determine the orientation of an adsorbed molecule with respect to the surface relies on a good theoretical description of the process. Although some progress has been achieved in obtaining electronic excitation cross sections for few molecular systems, the models including the surface effects are still simple minded and imprecise for these purposes [23]. The transferability of pseudopotentials to molecular electronic excitation processes by electron impact may lead to a substantial progress in this field, because it would allow the inclusion of surface effects through a cluster technique.

Our conclusions on the problem of transferability of the LDA pseudopotentials to the HF molecular-structure calculations confirm the high hopes of BHS [18] and the conclusions of Woodward and Kunz [20]. In the process of studying this transferability we were able to formulate simple rules to reduce standard Gaussian basis sets of AE calculations, thus profiting from the fact that the pseudo-wave-functions are much smoother than the true ones. Our conclusions on the problem of transferability to the calculation of scattering cross sections are also very optimistic. Here we were able to make calculations in small computer workstations (3.0 Mflops) reproducing AE results obtained in much more powerful machines, and to obtain results for molecules formerly considered very large.

II. THEORY

A. The Schwinger multichannel method

The SMC method has been described previously [3–5] and we only review here some key features. In the SMC method, the variational expression for the scattering amplitude is

$$[f_{\mathbf{k}_i,\mathbf{k}_f}] = -\frac{1}{2\pi}\sum_{m,n}\langle S_{\mathbf{k}_f}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V|S_{\mathbf{k}_i}\rangle, \tag{2}$$

where

$$d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle \tag{3}$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP+PV)}{2} - VG_P^{(+)}V. \tag{4}$$

In the above equations $S_{\mathbf{k}_i}$ is the product of a target state and a plane wave, V is the interaction potential between the incident electron and the target, χ_m is an (N+1)-electron Slater determinant used in the expansion of the trial scattering wave function, $\hat{H}$ is the total energy of the collision minus the full Hamiltonian of the system, P is a projection operator onto the open-channel space defined by the target eigenfunctions, and $G_P^{(+)}$ is the free-particle Green's function projected on the P space.

In our formulation all of the matrix elements needed for the evaluation of the scattering amplitude can be computed analytically, except those involving the Green's function, i.e., $\langle\chi_m|VG_P^{(+)}V|\chi_n\rangle$, which are evaluated by numerical quadrature [11].

B. The pseudopotential implementation

The pseudopotentials of BHS are nonlocal and have the form

$$\hat{V}_{\rm PP} = \hat{V}_{\rm core} + \hat{V}_{\rm ion}, \tag{5}$$

where

$$\hat{V}_{\rm core} = -\frac{Z_v}{r}\sum_{i=1}^{2} c_i erf(\rho_i^{1/2} r) \tag{6}$$

and

$$\hat{V}_{\rm ion} = \sum_{n=0}^{1}\sum_{j=1}^{3}\sum_{l=0}^{2} A_{njl} r^{2n} e^{-\sigma_{jl} r^2} \sum_{m=-l}^{+l} |lm\rangle\langle lm|. \tag{7}$$

The set of parameters A_{njl}, σ_{jl}, c_i, and ρ_i are tabulated in the article of BHS [18].

In the HF calculations, the three-center integrals of the nuclear potential and two atomic orbitals

$$V_{\mu\nu}^{\rm nucl} = \int d\mathbf{r}\, \phi_\mu \left[-\frac{Z_C}{r}\right] \phi_\nu \tag{8}$$

are replaced by the three-center integrals of the pseudopotential

$$V_{\mu\nu}^{\rm PP} = \int d\mathbf{r}\, \phi_\mu \hat{V}_{\rm PP} \phi_\nu, \tag{9}$$

and in the SMC calculations the nuclear hybrid integrals of the nuclear potential and one atomic orbital and a plane wave

$$V_{\mathbf{k}\nu}^{\rm nucl} = \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \left[-\frac{Z_C}{r}\right] \phi_\nu \tag{10}$$

are replaced by the nuclear hybrid integrals of the pseudopotential

$$V_{\mathbf{k}\nu}^{\rm PP} = \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{V}_{\rm PP} \phi_\nu. \tag{11}$$

In our calculations, the atomic orbitals were expanded in terms of Cartesian Gaussian functions

$$\chi_{lmn}^{\alpha\mathbf{A}}(\mathbf{r}) = N_{lmn}(x-A_x)^l (y-A_y)^m (z-A_z)^n e^{-\alpha|\mathbf{r}-\mathbf{A}|^2}. \tag{12}$$

With this choice the three-center and nuclear hybrid integrals of the pseudopotential are evaluated analytically.

Finding analytical expressions for the three-center integrals involving a nonlocal potential (defined in terms of spherical harmonics, Gaussian functions, and error functions) and two off-center Cartesian Gaussian functions is tedious but straightforward. The analytical expressions have been published elsewhere [24], though the expressions we used were differently defined, based on the real spherical harmonics and their coupling coefficients with the Cartesian polynomial part of the Gaussian functions, instead of the Clebsch-Gordan coefficients. The analytical expression for the nuclear hybrid integrals were obtained in a similar way.

III. TRANSFERABILITY TO MOLECULAR STRUCTURE CALCULATIONS

We made HF structure calculations for the molecules C_2, N_2, F_2, BH, NH, HF, CO, BF, H_2O, CH_2O, CH_4, NH_3, C_2H_4, SiH_4, Si_2C, and GeH_4. For AE calculations we used the Cartesian Gaussian primitive basis of Huzinaga [25] with contracted coefficients given by Dunning [26] ((9S5P)/[4S2P]). The Cartesian Gaussian functions used for SiH_4, Si_2C, and GeH_4 were (11S7P2D) on Si, (11S7P1D)/[6S4P1D] on Si, and Slater-type orbitals with each basis function begin expressed in terms of three Gaussian functions (STO-3G) on Ge and H, respectively. For each molecule, we made the AE calcu-

TABLE II. Ground-state eigenvalues (hartree).

Orbital	AE	PP full	PP red	Orbital	AE	PP full	PP red
	N_2				H_2O		
$2\sigma_g$	-1.5282	-1.5263	-1.5315	$2a_1$	-1.3613	-1.3536	-1.3561
$2\sigma_u$	-0.7723	-0.7638	-0.7688	$1b_2$	-0.7165	-0.7166	-0.7111
$1\pi_u$	-0.6264	-0.6335	-0.6278	$3a_1$	-0.5668	-0.5674	-0.5633
$3\sigma_g$	-0.6246	-0.6287	-0.6240	$1b_1$	-0.5063	-0.5007	-0.4956
	CO				C_2H_4		
3σ	-1.5905	-1.5909	-1.5958	$2a_g$	-1.0584	-1.0541	-1.0625
4σ	-0.8017	-0.8018	-0.8005	$2b_{1u}$	-0.8068	-0.8019	-0.8056
1π	-0.6645	-0.6721	-0.6650	$1b_{2u}$	-0.6580	-0.6618	-0.6563
5σ	-0.5495	-0.5487	-0.5477	$3a_g$	-0.6018	-0.6060	-0.5998
	CH_4			$1b_{3g}$	-0.5134	-0.5175	-0.5138
$2a_1$	-0.9582	-0.9570	-0.9621	$1b_{3u}$	-0.3808	-0.3825	-0.3766
$1t_2$	-0.5509	-0.5528	-0.5485				
					Si_2C		
	SiH_4						
				$6a_1$	-0.9052	-0.9027	-0.9074
$3a_1$	-0.7376	-0.7418	-0.7406	$5b_2$	-0.6269	-0.6349	-0.6325
$2t_2$	-0.4859	-0.4879	-0.4871	$7a_1$	-0.4407	-0.4434	-0.4446
	GeH_4						
				$6b_2$	-0.3571	-0.3640	-0.3629
$5a_1$	-0.7247	-0.7662	-0.7664	$2b_1$	-0.3532	-0.3567	-0.3542
$4t_2$	-0.4853	-0.4951	-0.4969	$8a_1$	-0.3472	-0.3513	-0.3493

TABLE III. Vertical excitation energies (hartree).

Molecule	State	AE	PP red
N_2	$^3\Pi_g$	0.2782	0.2732
	$^1\Pi_g$	0.3441	0.3407
H_2O	$^3B_1$	0.2732	0.2741
	$^1B_1$	0.3027	0.3054
	$^3A_2$	0.3610	0.3551
	$^1A_2$	0.3776	0.3719
SiH_4	$^3T_2$	0.3456	0.3483

lation and two pseudopotential calculations: one used the full Dunning basis (PP full), the other used that basis but with all Cartesian Gaussian functions with α [see Eq. (12)] greater than 10.0 (13.0 for F) removed (PP red). Thus we could exemplify how drastically one can remove the fast oscillations of the wave functions in the pseudopotential method. In Tables II–IV we present results for some typical cases. For each molecule we tabulate the orbital eigenvalues for the ground state, the vertical excitation energies and the vertical ionization potentials (in hartree). The results of three calculations are presented: the all-electron HF calculation (columns headed by AE), the full Dunning basis pseudopotential HF calculation (columns PP full), and the reduced Dunning basis pseudopotential HF calculation (columns PP red). [The PP red for SiH_4 and Si_2C follows the same criterion for the other molecules. For GeH_4 the PP red is a STO-3G potential which consists of (1S1P) on Ge.] One example of basis reduction is presented in Table V for oxygen, where, in the original Dunning basis, the coefficients for the Gaussian functions that are made zero are put in parentheses. The EE and the IP were calculated with the PP red only. In addition to the vertical excitation energies we also examined the spectrum of improved virtual orbitals (IVO) [27] for the singlet and triplet couplings, for these are used in inelastic-scattering calculations. For this we made a hole in the highest occupied molecular orbital to obtain the spectrum in the frozen core approximation by diagonalizing the V_{N-1} potential of the core in the self-consistent-field (SCF) basis. The agreement between the AE and PP spectra is very good (less than 2% error). This is also a good indication that the pseudopotential can be trusted in the calculation of excited states of molecules.

TABLE IV. Vertical ionization potentials (hartree).

Molecule	AE	PP red
N_2	0.5806	0.5807
CO	0.4905	0.4878
H_2O	0.4072	0.3963
CH_2O	0.3574	0.3563
Si_2C	0.3025	0.3040
CH_4	0.5067	0.5051
SiH_4	0.4705	0.4722
GeH_4	0.4726	0.4822

TABLE V. Oxygen Cartesian Gaussian functions.

Type	Expt.	Coeff.
S	7816.5400	(0.002 031)
S	1175.8200	(0.015 436)
S	273.1880	(0.073 771)
S	81.1696	(0.247 606)
S	27.1836	(0.611 832)
S	3.4136	0.241 205
S	9.5322	1.000 000
S	0.9398	1.000 000
S	0.2846	1.000 000
P	35.1832	(0.019 580)
P	7.9040	0.124 189
P	2.3051	0.394 727
P	0.7171	0.627 375
P	0.2137	1.000 000

The tables tell clearly that the LDA pseudopotential is transferable. The small deviations between the two PP results (Table II) are comparable to the deviations from the AE results. Much of these deviations may well be due to the fact that in neither case we have reached the Hartree-Fock limit. In fact, these deviations are very small, indicating that the nuclear potential can be successfully replaced by the pseudopotential, even using a poor Cartesian Gaussian expansion. In this process the core electrons are discarded and the wave functions become much smoother and easier to represent. This success is certainly outstanding because the LDA and HF schemes are so different and unrelated. Further, finding a "best" Gaussian basis is no difficult matter, because the tables show that even a simpleminded reduction of a standard basis will work.

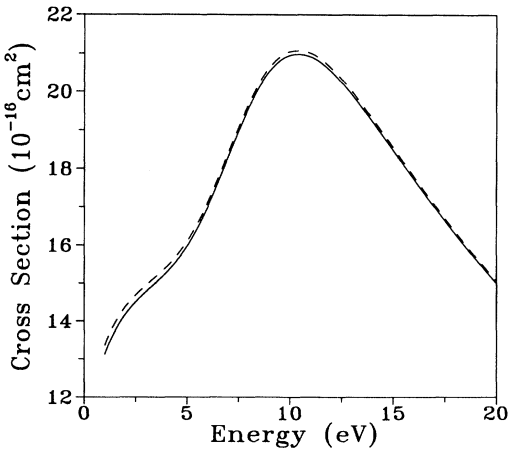

FIG. 1. Integral elastic cross section for CH_4. Solid line, present PP results; dashed line, AE SMC results.

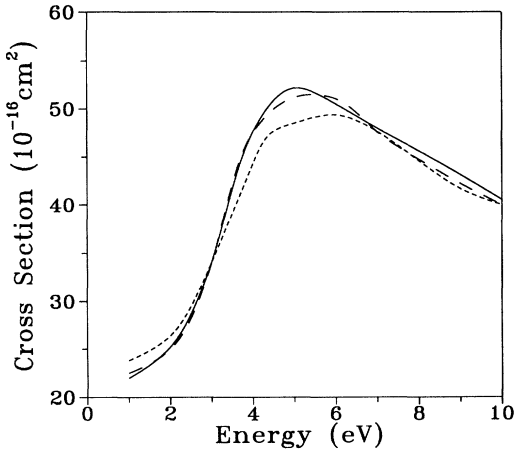

FIG. 2. Integral elastic cross section for SiH_4. Solid line, present PP results; dashed line, AE SMC results; short-dashed line, complex Kohn results.

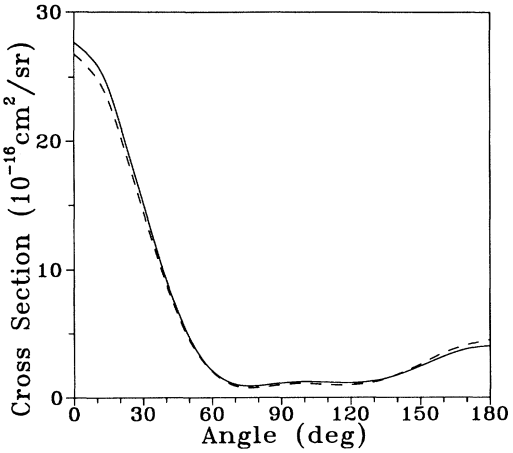

FIG. 4. Same as in Fig. 3 for SiH_4.

IV. TRANSFERABILITY TO SCATTERING CALCULATIONS

On the problem of scattering, our main goal was to verify if the physics of the electron-molecule collisions is reproduced by these PP, e.g., if the structures and shape resonances are present in the cross sections, and if their maxima occur at the same energies as in the AE calculation. We calculated integral and differential elastic cross sections for CH_4, SiH_4, GeH_4, and Si_2H_6 within the static-exchange approximation and some differential cross sections for electronic excitation by electron impact of the $^3A_2$ and $^1A_2$ states of CH_2O, using the SMC method as implemented with PP, and compared the results with previous all-electron SMC calculations [2, 28, 29] and others calculations available [30, 31].

In our calculations the PP were put on the C, O, Si, and Ge atoms, but the H atoms were treated as usual by the $1/r$ potential. The C, Si, and Ge atoms have four valence electrons and so the CH_4, SiH_4, and GeH_4 molecules have the same number of valence electrons and orbitals. The basis set and geometries that we used are the same as the previous AE calculations [2, 29]. We used in the basis set only those Cartesian Gaussian functions with α smaller than 10.0.

A. CH_4 and SiH_4

As a first test of our procedure we chose the CH_4 and SiH_4 molecules. For CH_4 we did both AE and PP calculations. In Figs. 1 and 2 we present our results for integral elastic cross sections for CH_4 and SiH_4, respectively. For SiH_4 we compare our results to that of Winstead and McKoy [28] and also to that obtained with the Kohn method [31]. The integral elastic cross sections obtained are in excellent agreement with the AE results. We also show in Figs. 3 and 4 differential elastic cross sections at 7.5 eV for CH_4 and SiH_4, respectively. The agreement between AE and PP calculations is again excellent.

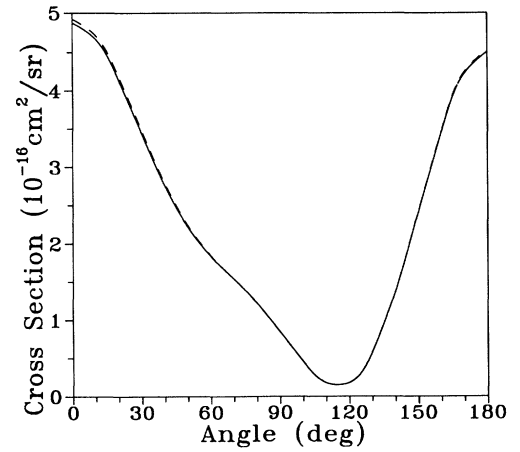

FIG. 3. Differential elastic cross section for CH_4 at 7.5 eV. Solid line, present PP results; dashed line, AE SMC results.

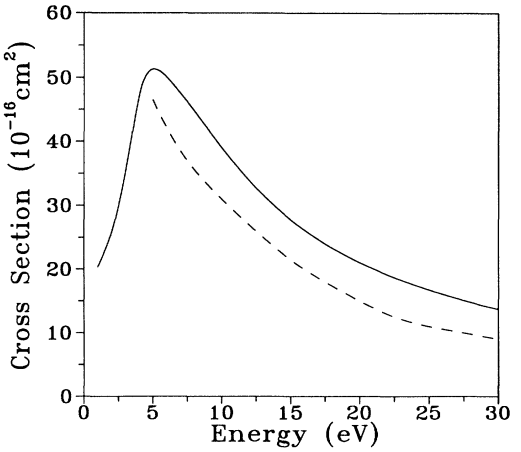

FIG. 5. Integral elastic cross section for GeH_4. Solid line, present PP results; dashed line, AE SMC results.

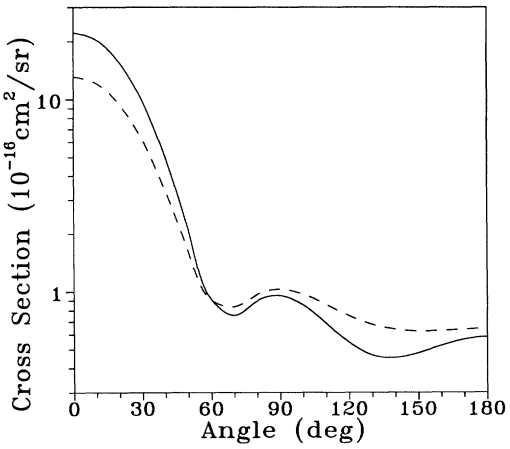

FIG. 6. Differential elastic cross section for GeH_4 at 15 eV. Solid line, present PP results; dashed line, AE SMC results.

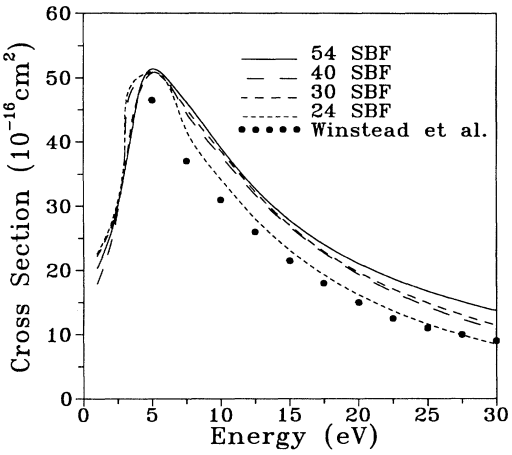

FIG. 7. Integral elastic cross section for GeH_4. Solid line, 54 scattering basis functions (SBF); long-dashed line, 40 sbf; dashed line, 30 sbf; short-dashed line, 24 sbf; solid circles, AE results.

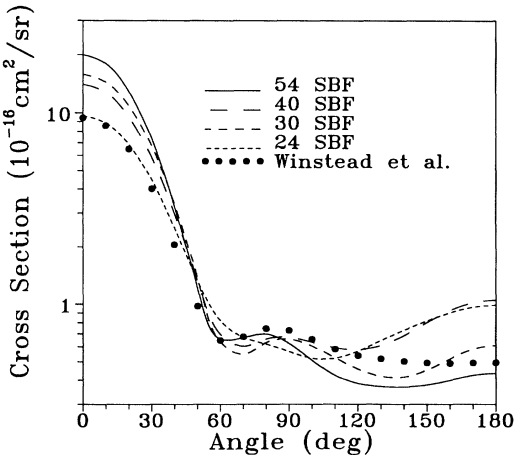

FIG. 8. Differential elastic cross section for GeH_4 at 20 eV. Labels as in Fig. 7.

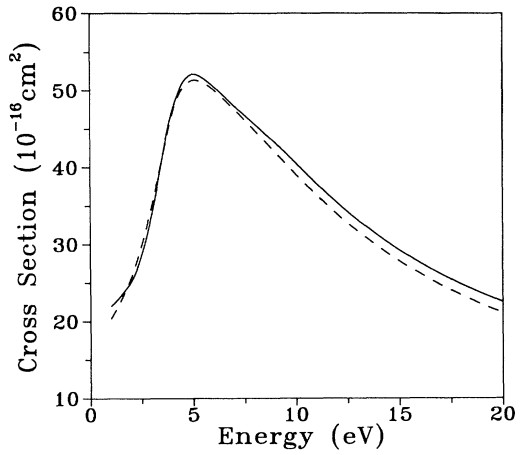

FIG. 9. Integral elastic cross section for GeH_4 and SiH_4. dashed line, GeH_4; solid line, SiH_4.

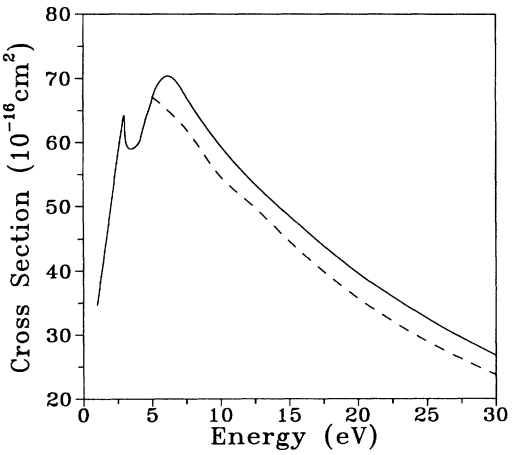

FIG. 10. Same as in Fig. 5 for Si_2H_6.

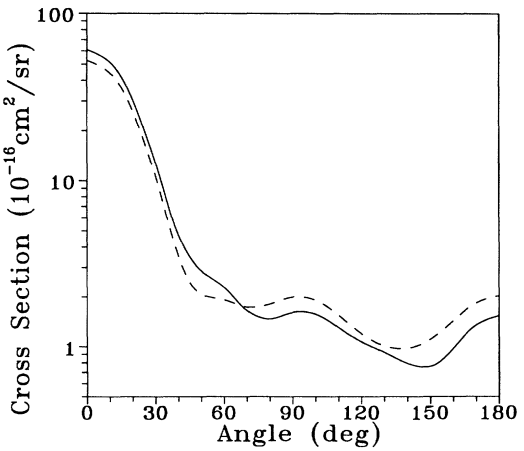

FIG. 11. Same as in Fig. 6 for Si_2H_6.

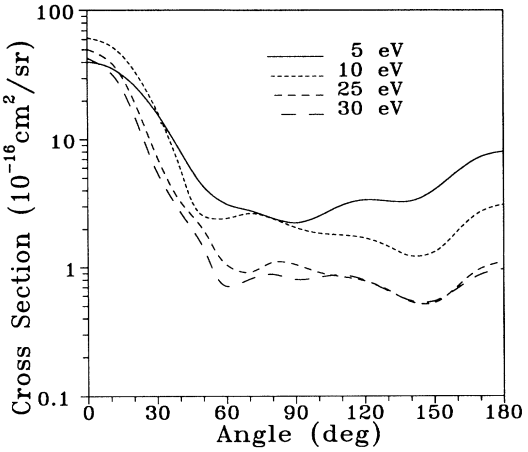

FIG. 12. Differential elastic cross section for Si_2H_6 at 5 eV (solid line), 10 eV (short-dashed line), 25 eV (dashed line), and 30 eV (long-dashed line).

B. GeH_4 and Si_2H_6

We also tested our procedures for the GeH_4 and Si_2H_6 molecules. In Figs. 5 and 6 we present our results for GeH_4 and compare them with the results of Winstead *et al.* [2]. For this system we made several calculations with different number of functions in the basis set to test the convergence of our results. Though all our results agree among them, they all lie about 20% below the AE calculation. In Figs. 7 and 8 we show some results of our test of convergence. We are sure that the best converged results are those with 54 scattering basis functions. Part of the difference might come from the PP including relativistic effects, while the AE calculation is nonrelativistic, but is also possible that the results of Winstead *et al.* are not fully converged.

In Fig. 9 we compare the SiH_4 and GeH_4 cross sections. The cross sections for these two molecules are very similar. The calculated valence eigenvalues and the experimental geometries are also very similar.

For Si_2H_6 we used the eclipsed instead of staggered conformation used by Winstead *et al.* [2]. Both results are in Fig. 10. The two curves are very similar, showing that electron scattering is unable to distinguish between the two conformations (neutrons would be needed).

In Figs. 11 and 12 we show the differential elastic cross sections at 15 eV and for 5, 10, and 25 eV for Si_2H_6, respectively. Again the AE (staggered) and PP (eclipsed) at 15 eV differ only in details.

C. CH_2O

We show in Figs. 13(a)–13(d) our differential cross sections for electronic excitation of the $^3A_2$ and $^1A_2$ of CH_2O for 15, 20, 25, and 30 eV, respectively. These results were obtained in a three-state calculation with a small basis set (with no additional functions for the expansion of the scattering wave function) which was sufficient to describe the SCF orbitals and the scattering above 10 eV. The wave functions for the $^3A_2$ and $^1A_2$ states were obtained using the IVO approach and the corresponding vertical excitation energies were 4.067 and 4.786 eV for the triplet and singlet, respectively. The corresponding experimental values are 3.45 and 4.26 eV and the AE excitation energies are 4.077 and 4.801 eV for the triplet and singlet states, respectively. Our differential cross sections are in perfect agreement with recent SMC [29] calculations and the Kohn-method [30] results, both also made in a three-state level of approximation. These results give an indication that our scheme may also be used to investigate electronically molecular excitation by electron impact.

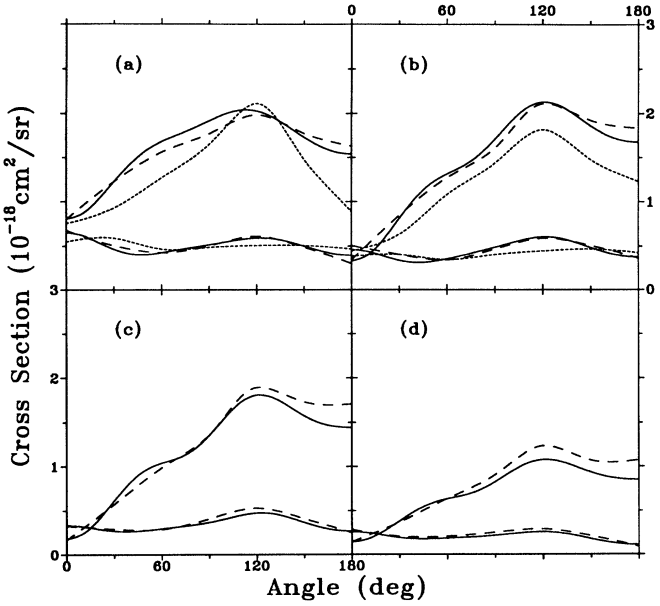

FIG. 13. Differential excitation cross section for CH_2O (a) at 15 eV. Solid lines, present PP results; dashed line, AE SMC results; short-dashed line, complex Kohn results; (b) same as in (a) at 20 eV; (c) same as in (a) at 25 eV, except that there are no Kohn results; (d) same as in (c) at 30 eV.

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