

Molecular Electric Polarizabilities*

II. Static Polarizabilities of Diatomic Molecules Using 2- ζ Quality EFV GTO Basis Set

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The electric field variant (EFV) Gaussian basis sets of double-zeta (2- ζ) quality are used for the calculation of the electric dipole polarizabilities of diatomic molecules in the Hartree-Fock approximation. The explicit external electric field dependence of the GTO basis set, introduced according to the method described in Part I of this series, is shown to account for the major portion of the electric field induced deformation of the wavefunction. The polarizabilities obtained in the present calculations are quite close to the best Hartree-Fock results. The deviations from near-Hartree-Fock values amount to 3–8 per cent for the parallel component and to 10–15 per cent for the perpendicular one. It was also shown that the same method leads simultaneously to a considerable improvement of the dipole moments.

Key words: Electric field variant Gaussian orbitals – Molecular polarizabilities – Molecular dipole moments – SCF perturbation theory

1. Introduction

In recent years the calculation of fairly accurate SCF energies for small and medium size molecules became more or less a routine work [1]. It is also believed that for several qualitative studies, concerned primarily with molecular energies, using relatively small basis sets provides a reasonable compromise between the computational effort and the accuracy of the computed quantities [2–4]. The progress in the SCF HF calculations for unperturbed systems has evidently stimulated an increasing interest in the possibility of perturbation calculation of the second- and higher-order molecular properties [5–9].

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It is widely recognized that using the standard small or medium size basis sets is not sufficient even for the calculation of the first-order molecular electric properties [2–4, 10, 11]. A straightforward basis set extension [12], if not accompanied by the property-directed choice of orbital exponents [13] or their optimization [5, 6], does not lead to encouraging results [12]. Moreover, despite the progress in computer technology, large bases introduce rather severe limitations for the size of the considered systems.

Recently, Werner and Meyer [13] have presented the results of very accurate polarizability calculations for a series of small molecules including the correlation effects. One has to be really impressed by the excellent quality of their results which was achieved mainly by the appropriate selection and, to some extent, optimization of the basis functions. However, the basis sets finally recommended by these authors make the list of molecules of a reasonable size rather short and in order to make the calculation of reliable molecular polarizabilities feasible for larger systems one has to look for much smaller bases.

It was recognized long ago that even relatively small basis sets may properly represent the perturbation effects provided they explicitly depend on the external perturbation [14]. For instance, the variable, magnetic field dependent bases proved to be very useful in the calculation of molecular magnetic properties [9, 15]. A similar idea lies behind very efficient methods for the calculation of molecular forces and force constants [16–20]. For the external electric field perturbation Moccia [21] proposed to multiply each atomic or molecular orbital by a common field-dependent factor. However, Moccia's exploratory calculations of the helium atom polarizability did not lead to very encouraging results. Also more extensive calculations performed by Dodds [22] did not prove that Moccia's proposal sufficiently accounts for the perturbation effects.

Recently, an alternative form of the explicit electric field dependence of the basis set functions was suggested [23]. These so-called electric field variant (EFV) basis sets have been constructed by using some inherent features of Gaussian functions following from the harmonic oscillator theory. The pilot numerical calculations for the hydrogen molecule [23] have shown a surprisingly high efficiency of the EFV GTO basis sets. These results seem to indicate a chance for a reliable calculation of molecular electric polarizabilities using relatively small field-dependent bases.

It seemed to be interesting to try the idea of EFV GTO's with one of standard, medium size Gaussian sets currently in use. For this purpose the basis set of Basch and Snyder [2] was selected and the electric dipole polarizabilities of a series of diatomic molecules were computed. It was also observed that the dipole moments computed using the EFV GTO's are considerably better than those calculated from the field-independent bases.

The polarizability results reported in this paper correspond to the SCF HF approximation. Werner and Meyer estimated [13] the correlation contribution to molecular electric polarizabilities as usually less than 10 per cent. This important

conclusion seems to confirm the previous belief that the near-HF values would probably be adequate for qualitative purposes [5, 6].

2. Electric Field Variant (EFV) GTO's

The computational convenience of the Gaussian-type orbitals is obviously the most important aspect of their usefulness in molecular calculations [24]. However, one can also exploit to some extent the fact that the GTO's are directly related to the solutions of the harmonic oscillator problem. Since the exact solution of the electric field perturbed harmonic oscillator is known, this provides at least a general idea about the analytic form of the perturbation dependence of Gaussian basis sets.¹

The harmonic oscillator embedded in the external static electric field F has the solutions of the same analytic form as for the unperturbed problem but corresponding to the shifted equilibrium position. If k denotes the harmonic force constant and the oscillator is assumed to represent an oscillating electron with the charge -1 a.u., then the equilibrium position shift for the external field applied along the μ 'th axis is given by

$$\Delta r_v(F_\mu) = -\delta_{\mu v} \frac{F_\mu}{k} = -\delta_{\mu v} \frac{F_\mu}{4\alpha^2} \quad (1)$$

where $\alpha = \frac{1}{2}\sqrt{k}$ can be easily identified with the GTO exponent.

It is quite obvious that one cannot treat each GTO of the Gaussian basis set as a separate oscillator solution, completely neglecting other terms of the molecular Hamiltonian. To account for these differences and in order to make the field dependence of the origin shift (1) more flexible, an additional parameter λ was introduced [23]. It was proposed that for the external electric field F_μ , applied along the μ 'th positive direction, the original unperturbed GTO basis set $\{\chi_i(\mathbf{r}; \alpha_i)\}$ becomes field dependent, i.e.,

$$\{\chi_i(\mathbf{r}; \alpha_i)\} \longrightarrow \{\chi_i(\mathbf{r}'(\lambda_\mu, F_\mu, \alpha_i); \alpha_i)\} \quad (2)$$

for each GTO χ_i , and

$$r'_v(\lambda_\mu, F_\mu, \alpha_i) = r_v - \delta_{\mu v} \lambda_\mu \frac{F_\mu}{\alpha_i^2} \quad (3)$$

The parameter λ_μ was assumed to be the same for all GTO's in a given basis set and then determined variationally for each physically different direction of the external field. Its directional properties reflect the fact that the degree of incompleteness of a finite basis set from the point of view of a direction-dependent perturbation will not be, in general, isotropic [26].

¹ The present paper is concerned with the electric field perturbation. However, a similar reasoning can also be used for several other perturbations [25]. Thus, the method outlined here has a rather general character and can be employed as a generator of variable bases for a number of important physical properties.

The proposed form of the external electric field dependence of GTO's completely agrees with a simple physical picture of the perturbation effects. The origin shift simply represents a field dependent polarization of a given orbital. The degree of this polarization will be large for outer orbitals (small GTO exponents) and negligibly small for the inner shell ones (very large exponents). As discussed previously [23], one can also rather safely assume that the field dependence of orbital exponents should be of minor importance.

The properties of the field dependent GTO's can be also discussed in terms of their expansion into the following series

$$\chi_i(F_\mu) = \chi_i(0) + F_\mu \chi'_{i,\mu}(0) + \frac{1}{2} F_\mu^2 \chi''_{i,\mu\mu}(0) + \dots \quad (4)$$

and then Eq. (3) gives a plausible idea about the original basis set extension for the calculation of perturbed energies [27]. As shown by our pilot calculations for H_2 , this indirect extension of the original basis set properly accounts for the external electric field induced polarization of the electron density distribution [23].

Using the perturbation dependent basis sets makes necessary some extension of the standard perturbation methods [28–30]. For the calculation of lower order perturbed energies one can also use the so-called finite field perturbation methods [31–33]. The computational aspects and details of our calculations are discussed in the next section.

3. Details of Numerical Calculations

The perturbation theory at the SCF HF level leads to the so-called coupled Hartree–Fock (CHF) perturbation schemes [28–30]. As far as the considered molecular electronic state is non-degenerate virtually the same results follow from the numerical differentiation of the total SCF energy computed at several, presumably small, values of the external perturbation strength. This numerical approach is usually referred to as the finite (field) perturbation method. Although this technique is obviously less elegant than the analytic CHF approach, it may be easier from the computational point of view [31–33]. However, using the finite perturbation techniques may result in rather difficult numerical problems because of the requirement of a very high precision of all intermediate calculations. Nevertheless, computing the second-order perturbed energies appears to be rather feasible.

A general density matrix formulation of the SCF perturbation theory for non-orthogonal, variable bases has recently been given by Dodds *et al.* [34]. The calculation of the second-order perturbed energies involves the first- and second-order derivatives of all one- and two-electron integrals. Even for the (*sp*) GTO bases this would lead to two-electron integrals involving *d*- and *f*-type Gaussians. Thus, using the numerical approach seems to be preferred. It should be pointed out that the accuracy of the finite field approach was previously checked [23] against the results of the analytic CHF calculations. It was found that the external field values

of the order of 0.005–0.01 a.u. give a completely acceptable accuracy of the numerically computed polarizabilities.

The numerical approach to the calculation of molecular polarizabilities requires much higher accuracy of the total SCF energy than in the standard SCF calculations. Thus the corresponding convergence limits were set up as 10^{-11} – 10^{-10} a.u., depending on the external field value. This corresponds to the density matrix threshold of the order of 10^{-7} – 10^{-6} .

For each physically different direction of the external electric field the EFV GTO basis set, as defined by Eqs. (2) and (3), introduces an additional parameter λ which has to be determined. It was shown [34] that for the EFV GTO's the second-order energy is a parabolic function of λ_μ . Because of the variation bounds [35] for the diagonal elements of the tensor-type second-order energy functionals, the optimal value of λ_μ can be simply obtained from the minimum condition for $E_{\mu\mu}^{(2)}(\lambda_\mu)$ [34]. This method was used throughout this paper. The parabolic fits for the diagonal second-order energies $E_{\mu\mu}^{(2)}(\lambda_\mu)$ were found to be almost exact, independently of the chosen set of points. This observation provides a further confidence in the numerical accuracy of our results.

The numerical determination of the optimal value of λ requires the repeated calculation of the field dependent SCF energies, and then the corresponding second-order energies, until the minimum of $E_{\mu\mu}^{(2)}$ with respect to λ_μ is located. In this respect it is worth attention that the parameter λ_μ enters the orbital origin shifts (2) in a product with the field strength. Thus, for a rough determination of the best value of λ_μ one can use the same integral files in a series of SCF calculations for different but close field values. This technique evidently speeds up the optimization process and was widely used during the calculations reported in this paper. Once the approximate value of optimal λ_μ was determined, all calculations were repeated with higher accuracy. In this way, the optimization process does not appear to be very time consuming. Moreover, as shown in the next section, there is a good chance for the use of some preselected values of λ_μ for the basis sets of a given quality.

The present calculations of the polarizability of a series of diatomic molecules were carried out using the EFV GTO basis sets derived from the (*sp*) sets of Basch and Snyder [2]. These in turn were composed of the contracted *s*-type Gaussians (CGTO's) obtained by Whitten [10] in the atomic SCF calculations, and contracted *p*-type Gaussians of Huzinaga [37]. For the hydrogen atom the basis set consists of 2 CGTO's (4 GTO's, [4/3.1]) and of 10 CGTO's (10 *s*-type GTO's contracted to 4 CGTO's [10/3.4.2.1], 5 *p*-type GTO's for each direction, contracted to 2 CGTO's [5/4.1]) for the first-row atoms (B–F). Although the basis sets recommended by Snyder and Basch [2] represent the so-called 2- ζ quality, they do not appear to be fully optimized since the *s* and *p* subsets were taken from different sources.

All calculations reported in this paper have been performed using CDC CYBER 72 computer.

4. Dipole Polarizabilities of Diatomic Molecules

Because of symmetry of diatomic molecules there are only two independent diagonal components of the polarizability tensor, i.e., the parallel (α_{\parallel}) and the perpendicular (α_{\perp}) one, which both define the rotational average $\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ and the polarizability anisotropy $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$. These two quantities are usually derivable from the experimental data, and therefore, our results are given in terms of α and $\Delta\alpha$.

The first series of calculations was performed with the field independent basis sets using the standard density matrix perturbation theory [28, 30]. For the field independent bases the corresponding finite perturbation calculations were carried out simultaneously and a comparison of the second-order energies derived from these two approaches led to the estimates of the appropriate external field strength. It was found that the computed polarizabilities agree within 10^{-3} a.u. for the field strength of 0.005–0.01 a.u. These estimates of a reliable field strength were very helpful in the numerical procedure used for the field dependent bases.

The results of the field independent basis set calculations as well as the λ -optimized polarizabilities obtained using the EFV GTO's derived from the Snyder–Basch 2- ζ sets are shown in Table 1. They are compared with 1) the best CHF values, which seemingly represent the corresponding HF limits, 2) a variety of less accurate CHF and finite field SCF results, and 3) the available experimental data or accurate theoretical results (i.e. including the correlation effects).

Table 1. Polarizabilities of diatomic molecules from field independent ($\lambda=0$) and optimized EFV GTO (λ_{opt}) Snyder–Basch (SB) basis set calculations. A comparison with near-HF, less accurate CHF or finite perturbation (FPT) SCF, accurate (including correlation), and experimental results

Molecule ^b	Calculation	Polarizability (in a.u.) ^a		Ref.	
		α	$\Delta\alpha$		
BH	SB ($\lambda=0$)	18.01	−3.31	This work	
	SB (λ_{opt})	21.30	−1.11	This work	
	Near-HF	—	—		
	FPT SCF	21.07	−2.31	[38] ^c	
	Accurate Exp.	—	—		
FH	SB ($\lambda=0$)	1.83	3.28	This work	
	SB (λ_{opt})	4.33	1.65	This work	
	Near-HF		4.74	1.59	[39]
			4.90	1.28	[13]
			3.18	2.17	[12]
	CHF		4.04	1.91	[12]
		FPT SCF	4.78	1.40	[13]
	Accurate	5.59	1.27	[13]	
	Exp.	5.60	1.49	^d	

Table 1, *contd.*

Molecule ^b	Calculation	Polarizability (in a.u.) ^a		Ref.
		α	$\Delta\alpha$	
N ₂	SB ($\lambda=0$)	7.99	8.91	This work
	SB (λ_{opt})	10.90	6.23	This work
	Near-HF	—	—	
	CHF or FPT SCF	—	—	
	Accurate	—	—	
	Exp.	11.74 11.93	4.67	^e
F ₂	SB ($\lambda=0$)	5.14	13.05	This work
	SB (λ_{opt})	8.03	9.44	This work
	Near-HF	8.30	9.31	[41]
	CHF or FPT SCF	—	—	
	Accurate	—	—	
	Exp.	—	—	
CO	SB ($\lambda=0$)	9.36	5.30	This work
	SB (λ_{opt})	11.34	3.20	This work
	Near-HF	12.40	3.19	[13]
	FPT SCF	$\alpha_{11} = 14.24$		[42]
		12.29	3.28	[13]
	Accurate	13.13	3.91	[13]
	Exp.	13.34	3.58	^e
BF	SB ($\lambda=0$)	16.35	-3.39	This work
	SB (λ_{opt})	17.59	-3.86	This work
	Near-HF	—	—	
	FPT SCF	$\alpha_{11} = 15.93$		[42]
	Accurate	—	—	
	Exp.	—	—	

^a 1 a.u. = 0.148184 Å³ = 1.64867 · 10⁻⁴¹ C² m² J⁻¹ [36, 43].

^b Molecular geometries taken from Ref. [2].

^c CGTO basis set with *d*-type and *p*-type polarization functions on B and H, respectively.

^d Taken from Ref. [13].

^e Taken from Ref. [40].

As expected, the field independent basis sets of Snyder and Basch are completely insufficient for the calculation of reasonable values of molecular polarizabilities. Although the ground state field independent unperturbed energies are usually acceptable, the lack of higher GTO's considerably affects the quality of the computed electric properties. On the expense of the optimization of two additional parameters (λ_{\parallel} , λ_{\perp}) the EFV GTO's lead to molecular polarizabilities of surprisingly good quality. It should be pointed out that in contrast to the orbital exponent optimization for much larger basis sets, as advocated by Lipscomb and his coworkers [6], the λ parameter optimization for much smaller bases is several orders of magnitude faster. The fact that the polarizabilities are quadratic functions of λ [34] is also a very convenient computational feature of the method.

The present results obtained using the EFV GTO basis sets of Snyder and Basch are evidently not as good as the best near-HF values of Lipscomb *et al.* [6] or Werner and Meyer [13]. However, they are usually better than the results of standard CHF calculations with large but non-optimized basis sets. According to our present experience the addition of polarization functions with standard orbital exponent does not help too much. It follows from Eq. (4) that for the present method to work properly, the original GTO basis set must include the valence-shell orbitals with rather low orbital exponents. They will introduce indirectly higher diffuse orbitals in the presence of the external field. Thus, one can conclude that the effectiveness of the EFV GTO perturbation approach requires a rather careful selection of the unperturbed SCF wave function. It is important that the tails of the SCF orbitals should be properly represented within a given basis set.

There is one striking feature of our results obtained using EFV GTO's. In contrast to the field independent basis set calculations, the optimization of the scale parameters λ_{\parallel} , λ_{\perp} makes the perturbed basis set more uniform. This optimization considerably reduces to non-equivalence of the original basis set for the parallel and perpendicular field direction. Most frequently the field independent sets led to acceptable values of the parallel component of the polarizability tensor. The perpendicular components were usually much worse and this resulted in very bad polarizability anisotropies. The λ -optimized EFV GTO values are in a very good agreement with the available near-HF results.

The optimized values of the parameter λ_{μ} are given in Table 2. For most of the molecules studied in this paper they are rather close to 0.1. It was also noticed that for either much smaller (BF) or much larger (BH) values of λ , the corresponding polarizability components do not exhibit a very substantial dependence on this parameter. This observation confirms our previous belief [23] that for basis sets of a given quality one can a priori assume a reasonable numerical value of λ . Some possible advantages of this observation will be further considered and illustrated in the last section of this paper.

Table 2. Optimized values of the parameter λ for the parallel and perpendicular component of polarizabilities of diatomic molecules. Snyder–Basch EFV GTO basis set

	BH	FH	N ₂	F ₂	CO	BF
λ_{\parallel}	0.165	0.113	0.097	0.075	0.094	0.059
λ_{\perp}	0.091	0.129	0.107	0.119	0.098	0.060

5. Dipole Moments of Diatomic Molecules

The first-order perturbed energy is a linear function of λ [34], and thus, it does not lead to any preferred value of this parameter. However, one can use the λ parameter values optimized for the second-order perturbed energy and this procedure happened to work unexpectedly well. Since the Hellmann–Feynman theorem is

Table 3. Dipole moments of diatomic molecules from field independent ($\lambda=0$) and optimized EFV GTO (λ_{opt}) Snyder–Basch (SB) basis set calculations. A comparison with near-HF and experimental data

Calculation	Dipole moment (in a.u.) ^{a, b}			
	BH	FH	CO	BF
SB ($\lambda=0$) ^c	0.806	0.935	0.163	-0.210
SB (λ_{opt}) ^d	0.613	0.737	0.122	-0.226
Near-HF	0.682 ^e	0.761 [42]	0.110 [42]	-0.243 [44]
		0.770 [13]	0.098 [13]	-0.347 [42]
Exp.	—	0.707 [45]	-0.044 ^f	—

^a 1 a.u. = 2.541 77 D = 8.47778 · 10⁻³⁰ C m [36, 43].

^b Polarity of the dipole moment is defined positive for A⁺B⁻ and H⁺A⁻.

^c This work. Recalculated data of Ref. [2].

^d This work. Computed for the optimized value of $\lambda_{||}$.

^e HF-limit estimate. Taken from Ref. [46].

^f Taken from Ref. [40].

violated² for the field dependent basis set [35], the EFV GTO's introduce some extra terms which account for the external electric field induced polarization of the original basis functions.

As shown by the data of Table 3, there is a quite substantial improvement of the dipole moment values due to the field dependence of the basis set. The dipole moments computed for the optimized values of $\lambda_{||}$ are fairly close to the results of near-HF calculations. On the other hand, in order to obtain near-HF dipole moments by using the Hellmann–Feynman theorem requires a considerable extension of the basis set and explicit inclusion of polarization functions. The effect of polarization functions is indirectly accounted for when using the EFV GTO's. It seems that within the present technique a further improvement of the computed dipole moments can be achieved by using slightly better unperturbed basis sets but still involving only the valance shell atomic orbitals. Nevertheless, as for the quality of the present basis sets the results obtained in this paper seem to be completely satisfactory.

6. General Discussion and Conclusions

As shown by the present results the explicit perturbation dependence of the basis set functions leads to a considerable improvement of the perturbed energy values and related molecular electric properties. However, the success of the method is mainly due to the optimization of the scale parameters λ . Although for medium size basis sets the corresponding optimizations can be performed within rather

² The dipole moment is defined by the first-order derivative of the field dependent energy with respect to the field strength and in general is not equal to the average value of the dipole moment operator computed with field dependent orbitals. For the same reason the polarizabilities have to be computed as the corresponding second-order derivatives of energy.

reasonable computing times, it would be evidently desirable to have some recommended values of λ . Moreover, since the proposed scheme should be feasible also for larger systems, the use of preselected values of λ appears to be quite important. For large molecules one can hardly request for such a high accuracy of all calculations as in the case of diatomics.

As already mentioned, the optimized values of λ were quite close to 0.1 for almost all of the considered molecules. Moreover, in the case of larger deviations the λ -dependence of molecular polarizabilities is rather insignificant, at least as far as one does not intend to obtain the best possible results. According to the data of Table 2 choosing λ as equal to 0.1 appears to be rather acceptable. The dipole moments and polarizabilities of diatomic molecules computed for $\lambda_{\parallel} = \lambda_{\perp} = 0.1$ are collected in Table 4. They are again compared with the results obtained for the field independent basis set and with the optimized ones. It follows from this comparison that using a non-optimized but properly selected value of λ may still result in a substantial improvement of the perturbed energies computed with the field independent bases. Obviously, the recommended value of the scale parameter λ will depend on the size and quality of the unperturbed basis set. However, the present results indicate that in principle one can determine the most appropriate mean values of λ for a series of molecules. Another possibility is to use the optimized values of λ selected from atomic calculation. This would make the present method even more feasible and applicable for polyatomic molecules. It should be pointed out that thus far there is no theoretical method providing reliable estimates of molecular polarizabilities for larger systems. It is a rather important feature of the EFV GTO approach that it works properly for comparatively small bases. This

Table 4. Dipole moments and polarizabilities of diatomic molecules. Results for field independent ($\lambda=0$), non-optimized ($\lambda=0.1$) and optimized (λ_{opt}) field dependent basis set of Snyder and Basch

Basis set	Molecule					
	BH	FH	N ₂	F ₂	CO	BF
	Dipole moment (in a.u.) ^a					
SB ($\lambda=0$)	0.806	0.935	—	—	0.163	-0.210
SB ($\lambda=0.1$)	0.689	0.760	—	—	0.119	-0.237
SB (λ_{opt})	0.613	0.737	—	—	0.122	-0.226
	Polarizability (in a.u.) ^b					
SB ($\lambda=0$)	18.01	1.83	7.99	5.14	9.36	16.35
SB ($\lambda=0.1$)	21.04	4.22	10.86	7.91	11.28	17.01
SB (λ_{opt})	21.30	4.33	10.90	8.03	11.34	17.59
	Polarizability anisotropy (in a.u.) ^b					
SB ($\lambda=0$)	-3.31	3.28	8.91	13.03	5.30	-3.39
SB ($\lambda=0.1$)	-1.83	1.78	6.02	9.41	3.20	-3.67
SB (λ_{opt})	-1.11	1.65	6.23	9.44	3.19	-3.86

^a See footnotes to Table 2.

^b See footnotes to Table 1.

feature seems to define clearly its usefulness and the range of its possible applications [47].

It is worth attention that a slight improvement of the unperturbed basis sets should lead to a further improvement of the computed dipole moments and polarizabilities, though one can hardly compete with the spectacular accuracy of the recent results of Werner and Meyer [13]. However, the results obtained for basis sets of 11 *s*-type and 7 *p*-type GTO's [48] indicated that a similar accuracy can be obtained also within the EFV GTO approach. The calculations presented in this paper were restricted to the SCF HF level. Obviously, one can use the EFV GTO basis sets within more advanced techniques as well. For instance, they seem to be quite suitable for the calculation of the correlation corrections to molecular electric properties. Moreover and rather unexpectedly they appear also to work properly in the case of hyperpolarizabilities. Finally, it should be mentioned that techniques similar to that exploited in the present paper are also expected to work for other perturbation operators [25].

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