An efficient implementation for determining volume polarization in self-consistent reaction field theory

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An efficient algorithm of the surface and volume polarization for electrostatics (SVPE) method in self-consistent reaction field (SCRf) theory, denoted by SV(1)PE, has been proposed to simulate direct volume polarization potential with a single layer of point charges outside the solute cavity while the indirect effects of volume polarization on surface polarization are still simulated with multiple layers of point charges. The free energies of solvation calculated using the SV(1)PE algorithm (implemented in GAUSSIAN03) reproduce the corresponding values calculated using the standard SVPE implementation within an error of only $\sim 0.1\%$ when the solute cavity is defined by the standard $0.001e/a_0^3$ solute charge isodensity contour. The SV(1)PE results are much less sensitive to the used cavity size in comparison with the well-established surface and simulated volume polarization for electrostatics [SS(V)PE] method which simulates volume polarization through an additional surface charge distribution on the cavity surface. The SCRf calculations using the SV(1)PE method are more efficient than those using the original SVPE method. © 2008 American Institute of Physics. [DOI: [10.1063/1.3020767](https://doi.org/10.1063/1.3020767)]

I. INTRODUCTION

Solvent effects play an essential role in chemistry and biochemistry because most chemical and biochemical reactions take place in solution. The experimental response of chemical, physical, and biochemical phenomena depends critically on solvent environment surrounding the molecules under consideration. While short-range nonelectrostatic interactions generally make significant contributions, in polar solvation the long-range electrostatic interactions between solute and solvent are often dominant.^{1–3} Self-consistent reaction field (SCRf) theory based on continuum model⁴ provides a very convenient approximate treatment of the electrostatic interactions in electronic structure calculations.³ SCRf theory considers the solvent to be a dielectric continuum medium which can be polarized by the solute leading to a reaction field that in turn polarizes the solute itself.¹ The reaction field is obtained from classical electrostatics by solving Poisson's equation to give a solute-solvent interaction potential included in the solute Hamiltonian.⁵ Most practical reaction field implementations describe the solvent polarization either explicitly or implicitly in terms of an apparent surface charge distribution on the solute cavity surface under the assumption that all solute charge density resides inside the cavity. However, unconstrained quantum mechanical calculation of the solute electronic structure always leads to a tail of the wave function penetrating outside the cavity, thereby causing an additional volume polarization in the reaction field.^{5,6} This polarization can be represented by an apparent volume charge distribution spread throughout the entire dielectric medium outside the cavity. It has been

demonstrated⁷ that neglecting charge penetration while retaining the simple dielectric continuum model leads to inconsistencies during the solution of Poisson's equation, and that most existing reaction field solutions are flawed by the inconsistencies.

The volume polarization was accounted for in several atomic and molecular calculations with spherical cavities in the past.^{6,8} A general implementation for an irregularly shaped solute cavity has been developed in our previous study.⁷ This general SCRf implementation is known as the surface and volume polarization for electrostatic interaction (SVPE). The SVPE is also known as the fully polarizable continuum model (FPCM) because it accurately evaluates both the surface and volume polarizations. The accuracy of results obtained from the numerical SVPE computation is related to the number of surface nodes N used to describe the surface polarization charge distribution on the cavity surface and to the number of layers M used to describe the volume polarization charge distribution outside the cavity. According to the SVPE implementation, if one could employ infinite number of surface nodes and infinite number of layers outside the cavity, then the calculated numerical results would be exactly the same as those obtained from the exact analytic solutions of Poisson's equation, provided that both are employed at the same quantum mechanical approximation level.⁷ Reported comparisons of the SVPE calculations with other SCRf calculations have shown that volume polarization effects have a significant influence on free energy of solvation and on other molecular properties.^{9,10}

Within the framework of SVPE implementation, the computing time increase for the *ab initio* SCRf calculation compared to the corresponding gas phase *ab initio* calculation has been found⁷ to be dominated by the evaluation of the

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one-electron integrals over the large number of point charges at the three-dimensional nodes that represent solvent polarization potential and that are included in the solute Hamiltonian, and therefore is approximately proportional to the total number of used nodes $N \times M$. In order to simplify the practical computation, simulation of volume polarization through a certain additional surface charge density has been considered theoretically and practically. Theoretically, the proposed simulation requires finding an additional surface charge distribution such that the associated potential reproduces the exact direct volume polarization effect on the solute-solvent interaction potential everywhere on and inside the cavity.⁵ However, the price paid for the simplification of utilizing an additional surface charge distribution in place of the correct volume polarization charge distribution is that the representation of the potential is erroneous outside the cavity. The simulation allows a much more concise approximate representation of volume polarization effects. The simulation approach is known as the surface and simulated volume polarizations for electrostatics [SS(V)PE] method.¹¹ Recently reported formal analyses^{11,12} of the simulation have also demonstrated that in the limit of infinite dielectric constant, the simulation of volume polarization effects is automatically included in the integral equation formulation of polarizable continuum model (IEFPCM) (Ref. 13) and the conductor-like screening model (COSMO).^{14–17} Specifically, one of the IEFPCM formalisms¹⁸ is accidentally equivalent to the SS(V)PE method. The COSMO method¹⁴ was also extended to simulate the effects of the escaping solute charge.¹⁷ The details on those theoretical extensions can be found in a concise review by Chipman.¹⁹

In the present study, we have developed a new, efficient computational algorithm of the surface and volume polarizations for electrostatics (SVPE) method to simulate direct volume polarization potential using a single layer of volume polarization charges outside the solute cavity surface while the indirect effects of volume polarization on surface polarization are still simulated by using multiple layers of the point charges. The new algorithm, denoted by SV(1)PE for convenience, has been implemented in GAUSSIAN03 program along with the original standard SVPE method. In the SV(1)PE implementation, the volume polarization charge distribution itself and the electric field generated by the volume polarization charge are calculated as described previously.⁷ However, the part of the solute-solvent interaction potential due to the volume polarization charge is simulated by a single volume layer. In this way, the electronic structure calculation using the SV(1)PE method only needs to evaluate the one-electron integrals over a single layer of volume polarization point charges associated with the direct contribution of volume polarization. The free energies of solvation calculated using the SV(1)PE implementation reproduce the corresponding values calculated using the original SVPE implementation within an error of only $\sim 0.1\%$ when the solute cavity is defined by the standard $0.001e/a_0^3$ solute charge isodensity contour.

II. METHOD

Following the notations of our previous paper,⁷ the solute Hamiltonian (H) in solution is described as sum of the solute Hamiltonian H^{vac} in vacuum and long-ranged solute-solvent electrostatic interaction potential energy V^{pol} ,

$$H = H^{\text{vac}} + V^{\text{pol}}. \quad (1)$$

Solvent is considered to be a homogeneous continuum medium with dielectric constant ϵ . It is polarized by the solute and produces a reaction field that in turn polarizes the solute itself. The SCRF method is used to treat the electrostatic interaction between the solvent and solute. The reaction field is obtained by solving Poisson's equation using boundary conditions on the cavity surface Γ . For a given solute charge density $\rho(\mathbf{r})$, full classical electrostatic potential is obtained as a solution of Poisson's equation

$$\Phi(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \begin{cases} 1, & \mathbf{r} \subseteq V^{\text{int}} \\ 1/\epsilon, & \mathbf{r} \subseteq V^{\text{ext}}. \end{cases} \quad (2)$$

Here V^{int} represents the space inside the cavity and V^{ext} refers to the space outside the cavity. Such volume separation naturally leads to the separation of the electrostatic potential into two parts vacuum potential $\Phi^{\text{vac}}(\mathbf{r})$ and reaction potential $\Phi^{\text{pol}}(\mathbf{r})$. Most of the practical implementations of reaction field theory neglect the volume polarization and approximate the reaction field potential only by the surface polarization arising from the discontinuity of the dielectric constant across the cavity surface. It can be described as a charge distribution $\sigma(\mathbf{s})$ on the cavity surface Γ , and it is proportional to the normal component of the electric field on the cavity surface,

$$\sigma(\mathbf{s}) = -\frac{\epsilon - 1}{\epsilon + 1} \frac{1}{2\pi} E_n(\mathbf{s}). \quad (3)$$

The approximation, in which the total electric field is the sum of electric fields produced by solute and by the surface polarization, i.e., $E_n(\mathbf{s}) = E_n^{\text{vac}}(\mathbf{s}) + E_n^{\sigma}(\mathbf{s})$, is true only if there is no solute charge outside the cavity. As discussed previously,⁷ the solute charge penetration through the cavity surface into the external region has two distinct contributions to the reaction potential Φ^{pol} . It contributes directly to the reaction potential through the volume polarization charge distribution $\beta(\mathbf{r})$ as given by

$$\Phi^{\beta}(\mathbf{r}) = \int_V \frac{\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \quad (4)$$

Here the volume polarization charge $\beta(\mathbf{r})$ is zero inside the cavity (internal region V^{int}) and is equal to $-[(\epsilon - 1)/\epsilon]\rho(\mathbf{r})$ outside the cavity (external region V^{ext}). Furthermore, it contributes to the reaction potential indirectly through an electric field, denoted by $E_n^{\beta}(\mathbf{s})$, generated by the volume polarization charge on the cavity surface Γ ,

$$E_n^{\beta}(\mathbf{s}) = -\frac{\epsilon - 1}{\epsilon} \int_{V^{\text{ext}}} \rho(\mathbf{r}) \frac{(n(\mathbf{s}) \cdot (\mathbf{s} - \mathbf{r}))}{|\mathbf{s} - \mathbf{r}|^3} d^3\mathbf{r}, \quad (5)$$

which affects the surface polarization charge distribution when solving the following equation to self-consistency:

$$\sigma(\mathbf{s}) = -\frac{1}{2\pi} \frac{\varepsilon - 1}{\varepsilon + 1} [E_n^{\text{vac}}(\mathbf{s}) + E_n^\sigma(\mathbf{s}) + E_n^\beta(\mathbf{s})]. \quad (6)$$

The details of the standard SVPE implementation have been described previously.⁷ In the present study, we focus on the approximate description of the effects of volume polarization with a significantly reduced computational cost compared to the standard SVPE method while providing sufficiently accurate values of the free energy of solvation ΔG ,

$$\Delta G = \Delta E^{\text{int}} + \frac{1}{2} \langle V^{\text{pol}} \rangle. \quad (7)$$

Here, ΔE^{int} is the change in internal energy of solute due to solvation. In recent studies^{11,12,19–21} the direct volume polarization is simulated as an additional surface polarization charge distribution on the cavity surface in order to reduce the computational cost. Such an approximate method is known as the SS(V)PE method. The approximation used in the SS(V)PE method is closely related to two other methods—the modified integral equation formalism (IEF) (Ref. 18) and conductor screening model COSMO.¹⁶ Both the IEF and COSMO methods were not developed to determine volume polarization effects or evaluate volume polarization charge density $\beta(\mathbf{r})$. Interestingly, Chipman's theoretical analysis^{19,21} revealed that the solutions of the practical equations used in the IEF and COSMO methods may also be considered to include an additional surface polarization charge distribution (on the cavity surface Γ) which approximately simulates volume polarization potential. As a result, the free energies of solvation ΔG are sensitive to the cavity size, and the actual results may deviate significantly from the corresponding SVPE results, especially for the calculations using a smaller cavity size.

The integration of the volume polarization charge is carried out in the external region V^{ext} outside the cavity surface Γ . In the previous study,⁷ the simple integration scheme (using regular mesh) required a very large number of the numerically discretized volume layers to be constructed in the external region. The brute-force computation techniques are very convenient for the systematic estimate of the computational errors and convergence rate. However, the practical computations are very demanding for larger molecules. The computational techniques that employ more efficient integration schemes in the SVPE method have been proposed by Chipman.²¹ The Gauss–Laguerre (GL) integration scheme dependent on the charge density decay exponent value was used, and in most cases a few layers of volume point charges would reproduce the results of the SVPE method using uniform grid of hundreds of volume layers.

The ultimate goal of the SVPE implementation development would be to use a single layer of the numerically discretized volume point charges β_i^M (located on the angular ray i) that satisfy the charge rule derived from the Gauss law for different solvents and behave properly for all cavity sizes. It was shown²² that this requirement cannot be satisfied exactly without actually calculating volume polarization charge $\beta(\mathbf{r})$. When additional surface charges $[\alpha_i(\mathbf{s})]$ are used to approximately account for the effects of the penetrating solute charge outside the cavity, the computational procedure in-

volves inversion of the integral operator and becomes unstable in the case of a complicated solute cavity.

In the present study, a single layer of the volume polarization charges (β_i^M) can be introduced to strictly satisfy the charge rule required by the well-known Gauss law. We have

$$\beta_i^M = \sum_{k=1}^M \beta_{ik}, \quad (8)$$

in which the discretized point charges β_{ik} (angular ray i and volume layer k) are calculated using multiple volume layers and reproduce the exact sum rule,

$$\beta_{ik} = -\frac{\varepsilon - 1}{\varepsilon} Q_{ik} \rho(\mathbf{r}_{ik}), \quad (9)$$

where the coefficients Q_{ik} 's contain the integration weights and surface elements. Instead of using inverting integral operator T [Eq. (32) in Ref. 2] in the SS(V)PE procedure, here in the SV(1)PE method we apply a local condition requiring that the single layer of point charges reproduces the same volume polarization potential $\Phi_i^\beta(x\mathbf{r}_{i0})$ in the internal region (here $\mathbf{r}_{i0}$ is ray i intersection with the cavity surface and x varies from 0 to 1) as the original multilayer SVPE point charges on the same ray i ,

$$\sum_{k=1}^M \frac{\beta_{ik}}{|\mathbf{r}_{ik} - x\mathbf{r}_{i0}|} = \frac{\sum_{k=1}^M \beta_{ik}}{|y_i\mathbf{r}_{i0} - x\mathbf{r}_{i0}|}. \quad (10)$$

The placement point $y_i\mathbf{r}_{i0}$ of the charge β_i^M can be easily calculated from the equation shown above in the following way:

$$y_i = x + \sum_{k=1}^M \frac{\beta_{ik}}{|\mathbf{r}_{i0}|} \left[\sum_{k=1}^M \frac{\beta_{ik}}{|\mathbf{r}_{ik} - x\mathbf{r}_{i0}|} \right]^{-1}. \quad (11)$$

It is convenient to choose the parameter x such that the average electric field on the cavity surface produced by the single layer of charges β_i^M will closely resemble the actual mean electric field produced by the multilayer volume polarization charges determined by using the standard SVPE method. Then, the Gauss law is satisfied in the same way used in the standard SVPE method using the multilayer volume polarization charges. Typically, the x values lie in a narrow range from 0.45 to 0.55 for numerous molecules (tested in the present study) using various cavity sizes. We finally chose the value of the empirical parameter x to be 0.5 for all of the SV(1)PE calculations discussed below.

The SV(1)PE method described above has been implemented in the GAUSSIAN03 program.²³ In the SV(1)PE implementation, the surface polarization charges are calculated in the same way used in the original SVPE method.⁷ For comparison, the standard SVPE and SS(V)PE methods using the multilayer volume polarization charges have also been implemented in the GAUSSIAN03 program, along with the surface polarization for electrostatics (SPE) method which completely neglects volume polarization.

TABLE I. Comparison of the free energy of solvation ΔG (kcal/mol) of NO^+ calculated using the SVPE method at the RHF/6-31G** level with the $0.001e/a_0^3$ isodensity contour using different volume charge integration schemes. The distance between layers is presented in the column "Step."

Integration	Number of layers	Step (Å)	ΔG
Original SVPE ^a	0	0.0125	-94.700 53
	321		-89.487 09
GL ^b	7	0.0125	-89.487 4
	6		-89.487 4
	5		-89.487 3
	4		-89.487 8
	3		-89.489 7
	2		-89.465 3
	1		-89.585 8
GL ($\xi=1$) ^c	10	0.0125	-89.488 9
	9		-89.488 7
	8		-89.487 4
	7		-89.484 4
	6		-89.481 0
	5		-89.485 0
	4		-89.517 3
	3		-89.607 3
	2		-89.727 7
	1		-89.561 0
Simpson 3/8 ^d	50	0.080	-89.488 7
	40	0.100	-89.488 7
	30	0.133	-89.488 6
	20	0.200	-89.488 1
	10	0.400	-89.477 4
Newton-Cotte (extended) ^e	30	0.133	-89.488 8
	20	0.200	-89.488 7
	10	0.400	-89.487 2
SV(1)PE	1	0.0125	-89.467 3
SS(V)PE-N ^f	5	0.0125	-89.485
	3	0.0125	-89.490
	2	0.0125	-89.504
	1	0.0125	-89.195

^aReference 7.

^bThe GL integration scheme used is the same as that used in Ref. 21. In the GL integration scheme, an integral $\int_0^\infty F(r)dr$ is approximated by the summation $\sum_i w_i F(g_i/\xi)/(\exp(g_i/\xi))$, where w_i and g_i are the GL quadrature weights and points, correspondingly.

^cThe special form of the GL integration scheme when $\xi=1$ in the above-mentioned formula.

^dThe commonly used Simpson 3/8 numerical integration rule over finite integration interval.

^eThe Newton-Cotte numerical integration rule.

^fReference 21.

III. NUMERICAL RESULTS AND DISCUSSION

The SV(1)PE implementation has been tested in practical SCRF calculations on some typical neutral, anionic, and cationic solutes in comparison with SVPE, SS(V)PE, and SPE implementations. Summarized in Table I are the solvation free energy (ΔG) values of NO^+ calculated at the RHF/6-31G** level with the $0.001e/a_0^3$ isodensity contour

FIG. 1. Computing time spent for the SPE, SVPE, and SV(1)PE calculations on CH_3CONH_2 using the $0.001e/a_0^3$ isodensity contour at the RHF/6-31G* level. Dielectric constant of 78.304 was used for water solvent. For volume polarization integration, the volume polarization charge was using uniformly positioned volume layers. Cavity surface was discretized using Lebedev set of 1202 points. The computing time is dependent on the number of layers used for the determination of volume polarization in both SVPE and SV(1)PE calculations.

cavity using different volume charge integration schemes. The GL integration scheme is very efficient, since it takes into account the analytical asymptotic behavior of the charge density. In our SV(1)PE implementation, the GL integration scheme is used in the same way used by Chipman.²¹ In nearly spherical molecules the decay exponents can be determined from the gradient values on the cavity. We noted that, in the case of more complex cavities, the determination of the solute charge density based on the use of the assumed single-exponent asymptotic behavior is unreliable and the GL integration scheme without using the assumed single-exponent asymptotic behavior is preferred. The uniform grid integration schemes such as Newton-Cotte and extended few-point integration schemes require a larger number of volume polarization layers to reproduce converged results. On the other hand, the GL integration is performed for the open $[\mathbf{r}_0, \infty]$ interval and is not suitable for the multiboundary extensions to the SVPE method. The SVPE method using GL integration scheme reproduces the converged results with at least five layers for nearly spherical solvation cavities, and at least 15 layers are required for more complex cavities. It is clear that the multilayer charge densities have to be evaluated before the construction of single-layer charges. Table I only includes results calculated for NO^+ , as the results obtained from the calculations on other solutes are similar concerning the performance of various integration schemes.

Depicted in Fig. 1 are the computing times spent for the electronic structure calculations using SPE, SVPE, and SV(1)PE methods on CH_3CONH_2 with Lebedev set of 1202 points and varying number of layers for the determination of volume polarization. The computing time is dependent on the number of layers used for the determination of volume polarization in both SVPE and SV(1)PE calculations. When only 15 layers were used, the volume polarization calculations on CH_3CONH_2 using the SVPE and SV(1)PE methods spent 149 and 78 s, respectively. The SV(1)PE volume polarization calculation was faster than the corresponding

TABLE II. Comparison of the solvation free energies (kcal/mol) of CN^- , NO^+ , H_2O , OCl^- , NH_4^+ , and CH_3CONH_2 calculated using the $0.001\text{--}0.030e/a_0^3$ isodensity contours relative to the calculated SVPE solvation free energy values listed in the last column. Dielectric constant of 78.304 was used for water solvent. For volume polarization integration, the volume polarization charge was discretized on 15 layers of point charges using GL integration scheme. Cavity surface was discretized using Lebedev set of 1202 points. Solvation free energies of NO^+ , NH_4^+ , H_2O , and CH_3CONH_2 were calculated at the RHF/6-31G** level, whereas solvation free energies of OCl^- and CN^- were calculated at the RHF/6-31+G** level.

Contour	Solute	SPE		SS(V)PE		SV(1)PE		SVPE
		Calc.	Dev.	Calc.	Dev.	Calc.	Dev.	
0.001	CN^-	-56.85	10.55	-67.32	0.08	-67.54	-0.14	-67.40
	NO^+	-94.70	-5.21	-89.51	-0.02	-89.47	0.02	-89.49
	H_2O	-8.65	-0.06	-8.58	0.01	-8.59	0.00	-8.59
	OCl^-	-58.54	9.87	-68.41	0.00	-68.52	-0.11	-68.41
	NH_4^+	91.48	-5.69	-85.80	-0.01	-85.76	0.03	-85.79
	CH_3CONH_2	-11.75	-0.29	-11.48	-0.02	-11.47	-0.01	-11.46
0.002	CN^-	-52.64	18.85	-71.07	0.42	-71.79	-0.30	-71.49
	NO^+	-109.03	-10.54	-98.49	0.00	-98.44	0.05	-98.49
	H_2O	-11.68	-0.09	-11.55	0.04	-11.60	-0.01	-11.59
	OCl^-	54.55	18.01	-72.39	0.17	-72.80	-0.24	-72.56
	NH_4^+	-104.78	-11.01	-93.75	0.02	-93.70	0.07	-93.77
	CH_3CONH_2	-15.97	-0.62	-15.27	0.08	-15.38	-0.03	-15.35
0.004	CN^-	-40.94	34.04	-76.23	1.25	-75.65	-0.67	-74.98
	NO^+	-132.02	-20.82	-111.08	0.12	-111.09	0.11	-111.20
	H_2O	-16.69	-0.09	-16.45	0.15	-16.63	-0.03	-16.60
	OCl^-	-43.78	32.86	-75.85	0.79	-77.21	-0.57	-76.64
	NH_4^+	-126.32	-21.33	-104.81	0.18	-104.85	0.14	-104.99
	CH_3CONH_2	-23.73	-0.54	-21.62	0.57	-22.31	-0.12	-22.19
0.010	CN^-	-56.48	21.22	-72.03	5.67	-79.87	-2.17	-77.70
	NO^+	-187.36	-49.32	-136.88	1.16	-137.78	0.26	-138.04
	H_2O	-31.63	-0.17	-30.46	1.00	-31.64	-0.18	-31.46
	OCl^-	-9.65	72.89	-78.15	4.39	-84.51	-1.97	-82.54
	NH_4^+	-182.83	-51.09	-130.38	1.36	-131.40	0.34	-131.74
	CH_3CONH_2	-50.70	-6.82	-39.67	4.21	-44.60	-0.72	-43.88
0.020	CN^-	62.28	143.78	-63.73	17.77	-87.08	-5.58	-81.50
	NO^+	-266.92	-93.28	-168.97	4.67	-174.26	0.38	-173.64
	H_2O	-64.10	-0.95	-59.22	3.93	-63.79	-0.64	-63.15
	OCl^-	45.89	137.77	-76.69	15.19	-97.18	-5.30	-91.88
	NH_4^+	-277.97	-99.71	-172.87	5.39	-177.63	0.63	-178.26
	CH_3CONH_2	-117.93	-25.18	-75.90	16.85	-95.39	-2.64	-92.75
0.030	CN^-	48.55	139.87	-56.23	35.09	-101.04	-9.72	-91.32
	NO^+	-344.95	-137.25	-197.75	10.04	-207.44	0.35	-207.79
	H_2O	-108.15	-2.56	-97.42	8.17	-106.74	-1.15	-105.59
	OCl^-	Failed ^a		-75.63	31.45	-116.66	-9.58	-107.08
	NH_4^+	-384.39	-149.82	-222.99	11.58	-233.55	1.02	-234.57
	CH_3CONH_2	-229.57	-66.74	-126.43	36.40	-168.51	-5.68	-162.83

^aThe SPE calculation using the $0.030e/a_0^3$ contour was not converged.

SVPE calculation by less than twofold when only 15 layers were used for CH_3CONH_2 . However, as one can see from the data in Fig. 1, the SV(1)PE calculation becomes more efficient relative to the corresponding SVPE calculation when the number of layers increases.

To evaluate how the present approximation performs compared to other methods, the results obtained from the SV(1)PE calculations can be compared with those from the SVPE, SS(V)PE, and SPE calculations on the same mol-

ecules. The results obtained from the standard SVPE calculations are used as the standard references. The solvation free energies listed in the Table II were calculated using cavities constructed as isodensity contours of solute charge density ranging from $0.001e/a_0^3$ to $0.030e/a_0^3$. For each charge isodensity value, the different rows refer to the solvation free energies of different molecules. The data in Table II clearly indicate that the solvation free energies calculated using the SV(1)PE method reproduce the corresponding values calcu-

TABLE III. Comparison of the solvation free energies (kcal/mol) of various molecules calculated using the $0.001e/a_0^3$ isodensity contour and different volume charge integration schemes. Dielectric constant of 78.304 was used for water solvent. For volume polarization integration, the volume polarization charge was discretized on 15 layers of point charges using GL integration scheme. Cavity surface was discretized using Lebedev set of 1202 points. Solvation free energies of NO^+ , NH_4^+ , H_2O , and CH_3CONH_2 were calculated at the RHF/6-31G** level, whereas solvation free energies of OCI^- and CN^- were calculated at the RHF/6-31+G** level.

	CN^-	OCI^-	NO^+	NH_4^+	H_2O	CH_3CONH_2
SPE ^a	-56.8528	-58.5421	-94.7005	-91.6970	-8.6717	-11.1262
Δ (%)	15.65	14.43	5.83	6.49	0.95	2.46
SVPE ^a	-67.4038	-68.4109	-89.4871	-86.1046	-8.5903	-10.8592
SVPE ^b	-67.4040	-68.4046	-89.4887	-86.1139	-8.5942	-10.8684
SS(V)PE	-67.3237	-68.4114	-89.5059	-86.1263	-8.5847	-10.8802
Δ (%)	0.11	0.00	0.02	0.02	0.06	0.19
SS(V)PE-1 ^c	-66.993		-89.195		-8.606	-10.872
Δ (%)	0.61		0.32		0.18	0.12
SV(1)PE	-67.5484	-68.5106	-89.4660	-86.0862	-8.5942	-10.8727
Δ (%)	0.21	0.14	0.02	0.02	0.04	0.12

^aReference 7.

^bPresent work (using the new GAUSSIAN03 implementation).

^cReference 21.

lated using the standard SVPE method within an error of only $\sim 0.1\%$ when the solute cavity is defined by the $0.001e/a_0^3$ solute charge isodensity contour. It is understandable that the deviations of the SV(1)PE results from the corresponding SVPE results increase by increasing the used solute charge isodensity contour value. We note that the previously used charge isodensity contour values for practical computational studies have been significantly smaller than $0.01e/a_0^3$.^{9,10,24} So long as the used charge isodensity contour value is smaller than $0.01e/a_0^3$, the SV(1)PE calculations still can accurately reproduce the SVPE results within a deviation less than 1% based on the data in Table II.

The data in Table III indicate that the contributions of volume polarization to the free energy of solvation (which can be considered to be the difference between the free energies of solvation calculated by using the SPE and SVPE methods) are $\sim 14\%$ or $\sim 16\%$ for the anions, $\sim 6\%$ for the cations, and $\sim 1\%$ or $\sim 2\%$ for the neutral molecules examined in this study. The SS(V)PE results are as good as the corresponding SV(1)PE results in comparison with the standard SVPE results when a charge isodensity contour value ($0.001e/a_0^3$ or $0.002e/a_0^3$) is used, as seen from the results summarized in Tables II and III. When the used charge isodensity contour value increases, deviations of the SS(V)PE results from the standard SVPE results increase significantly faster than the corresponding SV(1)PE results, as seen from the data in Table II. So, the SV(1)PE results are significantly closer to the corresponding SVPE results when a larger charge isodensity contour value is used in the calculations.

IV. CONCLUSION

The proposed single-layer volume polarization charge algorithm, i.e., SV(1)PE, provides a valuable alternative to the approximate methods accounting for both surface and volume polarizations in the SCRf calculations. The solvation free energies obtained from the SV(1)PE calculations accurately reproduce those from the standard SVPE calculations

within an error of only $\sim 0.1\%$ when the solute cavity is defined by the previously calibrated $0.001e/a_0^3$ solute charge isodensity contour. Furthermore, the results obtained from the SV(1)PE calculations are much less sensitive to the used cavity size, compared to the SS(V)PE method which simulates volume polarization through an additional surface charge distribution on the cavity surface. As the single-layer volume polarization point charges are placed away from the cavity surface and the SV(1)PE method produces similar electric field as the standard SVPE method, a much faster estimate of the electric field is immediately available using the single-layer volume polarization point charges. As a result, the electronic structure calculations using the SV(1)PE method are more efficient than those using the original SVPE method.

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