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Valence State Atoms in Molecules. 5. Universal Scaling of the Inner Branch of Fifty RKR Potential Energy Curves. Comparison of the Valence State, Morse, and Rydberg Curves

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Achieving an unprecedented degree of universality, the valence state potential energy curve (VS−PEC) reproduces the inner branch of 50 “experimental” RKR−PECs to an accuracy of 1.14% average unsigned deviation. The scaled RKR curves of 50 molecules with calculated partial charges, $0 \leq \delta < 0.9$, coalesce into virtually a single curve in the Coulson−Fischer range, $0.5\,R_e \leq R \leq 1.5R_e$, when plotted against $q_{VS} = z^{1/2}(R - R_e)/R_e$, with $z = \alpha_e\tilde{\nu}_e/2B_e^2$. The ground-state dissociation energy D_e can be predicted from the equilibrium spectroscopic constants B_e, $\tilde{\nu}_e$, α_e and the calculated VS promotion energy.

1. Introduction

In the previous parts of this series,[1−4] the foundations of the valence state atoms-in-molecules (VSAM) model have been developed and illustrated by several applications pertaining to the electronegativity (EN) and chemical hardness of valence state atoms and groups in molecules,[1,4] the universal VS potential energy function[2,3,5] with its transferable force constant increments, and the gas-phase electrophilicity of atoms and molecules.[4,6] We now report our results on the scaling properties of the VS potential energy curve (VS−PEC) and its performance in reproducing the inner (or repulsive) branch Rydberg−Klein−Rees[7] (RKR)[55] potential energy curves.

The detailed form of the repulsive branch of the diatomic potential energy curve is important for atomic and molecular collision processes,[8] the band shapes, and Franck−Condon factors of electronic spectra[9−11] and, of course, the vibrational or nuclear wave functions of the stationary molecular states. It also influences adhesion, cohesion, and chemisorption where similar potentials are operative.[12] The theoretical importance of the repulsive terms and the different behavior of the various PECs at small and very small distances have been repeatedly emphasized.[13−18] Varshni[16] and Tellinghuisen[17] quantitatively assessed the performance of a number of PE functions in predicting the inner branch. Jenč and Brandt[18] used their reduced potential curve method[19,20] for extrapolations of RKR data on the repulsive branch. Frost and co-workers[13] and Nalewajski and Parr[15] have discussed in detail the necessity for PE functions to approach positive infinity as the internuclear distance reaches $R = 0$. The VS−PE function[2,3] is among the select few to satisfy this criterion. Most of the well-known empirical functions including Morse[21] and Rydberg[22] fail to approach infinity at $R = 0$. A comparison of the performance of the reduced VS−PE, Morse, and Rydberg functions for $R \leq R_e$, the equilibrium internuclear distance, is used here to assess the impact of this criterion and to compare their abilities to predict the outer branch of the PEC based on a computed inner branch. Further comparisons up to $R \leq 1.5R_e$, which may be called the Coulson−Fischer range,[23] evaluate the theoretical suitability of the VSAM model.

2. Methods of Investigation

2.1. Valence State Atoms and Potential Energy Curves. A valence state atom (VSA) is conveniently described as an atom-in-a-molecule (AIM) devoid of all wave interference effects. We discuss the differences between a free atom in its ground state and a VSA following Ruedenberg’s analysis of chemical bonds and AIMs.[24] Describing the molecule in terms of reduced density matrices,[25,26] Ruedenberg separated the effects bonding has on the one-particle density $\rho(r)$ and the two-particle density, or electron-pair density $\pi(r_1, r_2)$. In the process of defining the VS, an intermediate reference state of the atoms forming the molecule is constructed. This promoted state PS has the same one-particle density matrix as the true correlated ground state of the molecule, but it contains no prejudicial information concerning electron correlation. The PS energy is above that of the ground state of the atom, since any deformation of the ground state density requires energy. To proceed from the PS to the reference VS, further modifications are needed, but they involve changes in the two-matrix only while keeping the one-matrix as it is in the PS.[4,24] The VS accounts for the increased on-site pair density of the AIM caused by “sharing penetration” or the presence of “ionic structures”.[24] Thus, the VSA is described by its electron density $\rho^{vs} = \rho^{ps}$ and pair density π^{vs}, which simultaneously fulfill

$$\rho_{mol} = \sum_A \rho_A^{vs} + \rho^{i} \tag{1}$$

and

$$\pi_{mol} = \sum_A \pi_A^{vs} + \pi^{i} \tag{2}$$

ρ^i and π^i are the interference contributions to ρ_{mol} and π_{mol}, respectively, and the summation is over all atoms A. The VSAs are generated by a dissociation process during which the interference-free densities ρ^{vs} and π^{vs} are kept “frozen” at the values they have in the molecule.[1−4,24] During such dissociation, all overlap-dependent interference densities vanish but the sharing penetration remains constant. The VS energy is higher than the PS energy due to the additional on-site sharing penetration retained from the molecule. On the basis of the bond analysis of Coulson and Fischer,[23] ρ^{VS} and π^{VS} are expected to remain quasi “frozen” up to $R \leq 1.5R_e$. Thus, the real dissociation process will differ from the one generating VSAs for $R > 1.5R_e$. Recently one of us (Szentpály) has condensed the essential steps of Ruedenberg’s analysis into a semiempirical valence state atoms in molecules (VSAM) model of bonding.[1−4]

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TABLE 1: Spectroscopic Constants, VS and Ground State Dissociation Energies for Diatoms[a]

molecule	partial charge, $\lvert\delta\rvert$	R_e/Å	k_e/eV Å^{-2} [b]	D_e/eV	D_{vs} /eV
		Homonuclear			
H_2	0	0.7413	35.94	4.747	11.17
Li_2	0	2.673	1.576	1.056	3.443
Na_2	0	3.079	1.071	0.735	3.042
K_2	0	3.924	0.613	0.520	2.472
Rb_2	0	4.175	0.521	0.492	2.338
Cs_2	0	4.648	0.434	0.453	2.164
C_2	0	1.312	59.47	6.27	22.36
Si_2	0	2.246	13.47	3.242	11.33
N_2	0	1.098	143.25	9.906	31.79
P_2	0	1.894	34.75	5.08	19.72
O_2	0	1.207	73.45	5.213	20.05
S_2	0	1.889	29.1	4.414	15.15
Cl_2	0	1.988	20.13	2.514	10.47
Br_2	0	2.281	15.397	1.991	9.15
I_2	0	2.666	10.764	1.556	8.59
		Hydrides			
LiH	0.473	1.596	6.404	2.515	5.933
NaH	0.498	1.887	4.878	1.98	5.26
KH	0.571	2.240	3.52	1.83	4.64
RbH	0.587	2.367	3.216	1.808	4.52
CsH	0.615	2.494	2.923	1.834	4.37
MgH	0.34	1.73	7.969	1.362	6.92
CaH	0.45	2.003	6.11	1.78	7.39
CH	0.08	1.124	27.95	3.65	9.51
SiH	0.3	1.52	14.95	3.185	7.89
NH	0.006	1.037	37.25	3.63	10.49
OH	0.175	0.971	48.39	4.62	11.95
SH	0.023	1.345	26	3.547	9.585
HF[c]	0.415	0.9168	60.24	6.12	13.54
HCl[c]	0.179	1.275	32.23	4.617	10.55
AgH	0.287	1.618	11.38	2.39	6.78
		Same Group Heteronuclear			
LiNa	0.034	2.885	1.306	0.876	3.214
ICl	0.151	2.321	14.89	2.177	9.555
IBr	0.098	2.469	12.91	1.834	10.11
		Sulphides and Oxides			
CS	0.196	1.535	53.12	7.435	21.35
SiS	0.38	1.929	30.91	6.466	19.34
NO	0.163	1.151	99.85	6.614	22.78
SO	0.173	1.493	51.78	5.427	18.76
SeO	0.214	1.648	41.01	4.59	17.54
		Metal Halides, Oxides, and Sulphides			
LiF	0.822	1.564	15.48	6.0	7.82
NaF	0.844	1.926	10.99	4.98	6.59
NaCl	0.814	2.361	6.788	4.29	5.71
BeF	0.625	1.361	35.06	6.24	13.29
MgF	0.708	1.750	19.49	4.67	10.64
AlF	0.785	1.654	26.42	6.94	9.23
GaF	0.782	1.774	21.26	6.021	8.36
GaCl	0.743.	2.202	11.41	4.955	7.05
AgCl	0.556	2.281	11.58	3.241	6.563
BeO	0.455	1.331	46.94	5.242	17.24
MgO	0.536	1.749	21.77	3.398	14.25
PbS	0.446	2.287	18.77	3.517	13.07

[a] Experimental R_e, k_e, and D_e are from refs 33, 34, 46, and 47. [b] Conversion factor: eV Å^{-2} = 16.02 Nm^{-1}. [c] 5% and 10% s character was used for F and Cl in the calculation of VS for HF and HCl, respectively.

TABLE 2: Spectroscopic Constants and Operational VS Dissociation Energy[a]

molecule	$10^3\ \alpha_e$/cm^{-1}	F_{obs}	D_{VS} (α_e)/eV	$D_{VS}^{(\alpha)}/D_{VS}$
		Homonuclear		
H_2	3076	0.609	10.81	0.968
Li_2	7.040	0.911	4.119	1.196
Na_2	0.868	0.963	3.516	1.155
K_2	0.212	1.036	3.037	1.229
Rb_2	0.045 ± 0.01	0.8 ± 0.2	2.78 ± 0.9	1.23 ± 0.3
Cs_2	0.023	1.18	2.64	1.22
C_2	17.65	1.648	20.71	0.926
Si_2	1.350	2.013	11.25	0.993
N_2	17.81	1.752	32.86	1.034
P_2	1.420	2.008	20.69	1.049
O_2	15.93	2.008	17.76	0.886
S_2	1.570	2.174	15.92	1.051
Cl_2	1.530	2.395	11.07	1.058
Br_2	0.313	2.565	10.41	1.138
I_2	0.114	2.914	8.752	1.019
		Hydrides		
LiH	216.5	0.898	6.055	1.02
NaH	135.3	1.100	5.263	1.00
KH	94.39	1.328	4.43	0.955
RbH	70.71	1.213	4.951	1.095
CsH	66.95	1.356	4.469	1.023
MgH	185.8	1.364	5.829	0.842
CaH	97.00	1.147	7.124	0.964
CH	530.0	1.210	9.728	1.023
SiH	219.0	1.325	8.689	1.101
NH	644.0	1.281	10.42	0.993
OH	714.0	1.248	12.19	1.02
SH	270.0	1.326	11.82	1.233
HF	795.8	1.250	13.50	0.99
HCl	307.2	1.365	12.80	1.213
AgH	201.2	1.420	6.99	1.031
		Same Group Heteronuclear		
LiNa	3.776	1.130	3.207	0.998
ICl	0.536	2.633	10.16	1.063
IBr	0.197	2.734	9.595	0.950
		Sulphides and Oxides		
CS	5.920	1.886	22.12	1.036
SiS	1.470	1.994	19.34	0.994
NO	17.80	1.944	22.67	0.995
SO	5.736	2.115	18.19	0.970
SeO	3.23	2.272	16.34	0.932
		Metal Halides, Oxides, and Sulphides		
LiF	20.29	1.700	7.425	0.950
NaF	4.559	2.134	6.368	0.965
NaCl	1.625	2.076	6.076	1.064
BeF	17.60	1.676	12.92	0.972
MgF	4.480	1.999	9.953	0.936
AlF	4.984	2.220	10.85	1.175
GaF	2.864	2.298	9.683	1.158
GaCl	0.7936	2.152	8.564	1.215
AgCl	0.596	2.256	8.797	1.380
BeO	19.0	1.728	16.04	0.930
MgO	5.0	1.984	11.192	0.785
PbS	0.435	2.30	14.23	1.090

[a] Experimental α_e values are from refs 33, 34, 46, and 47.

To achieve a maximum degree of universality in the treatment of AIMs, it is necessary to take the sum of their VS energies as the reference zero energy of the molecule. The theoretical significance of the VS energy of a single bonded homonuclear diatomic molecule manifests itself in the restricted Hartree−Fock (RHF) model. At large internuclear distances ($R \gg R_e$), the RHF−PEC of the diatom A_2 approaches

$$U(R) = 2[E(A) + {}^1/_4 J] - \frac{e^2}{8\pi\epsilon_o R} \qquad (3)$$

where J is the two-electron one-center repulsion energy of the active valence orbital and $E(A)$ the ground-state energy of the free atom. The energy ${}^1/_4 J = P^o$ per atom and bond is needed to reach the MO theoretical VS of the neutral atom.[1,2] For polar molecules, however, the VS correspond to partially charged atoms. At the RHF level, even slightly polar molecules dissociate into ions. Thus, the one-electron densities ρ^{VS} and pair densities π^{VS} do not, in general, remain constant along the RHF−PEC. In fact, the RHF dissociation limit coincides with the VS energy for the homonuclear case only. The concept of Valence State has been extended to charged AIMs by the introduction of the following semiempirical conditions: (i) the partial charges δ are calculated from VS electronegativity equalization (VSENE)[1] as

$$\delta_Y = 2(\chi_X{}^o - \chi_Y{}^o)/(J_X + J_Y) \qquad (4)$$

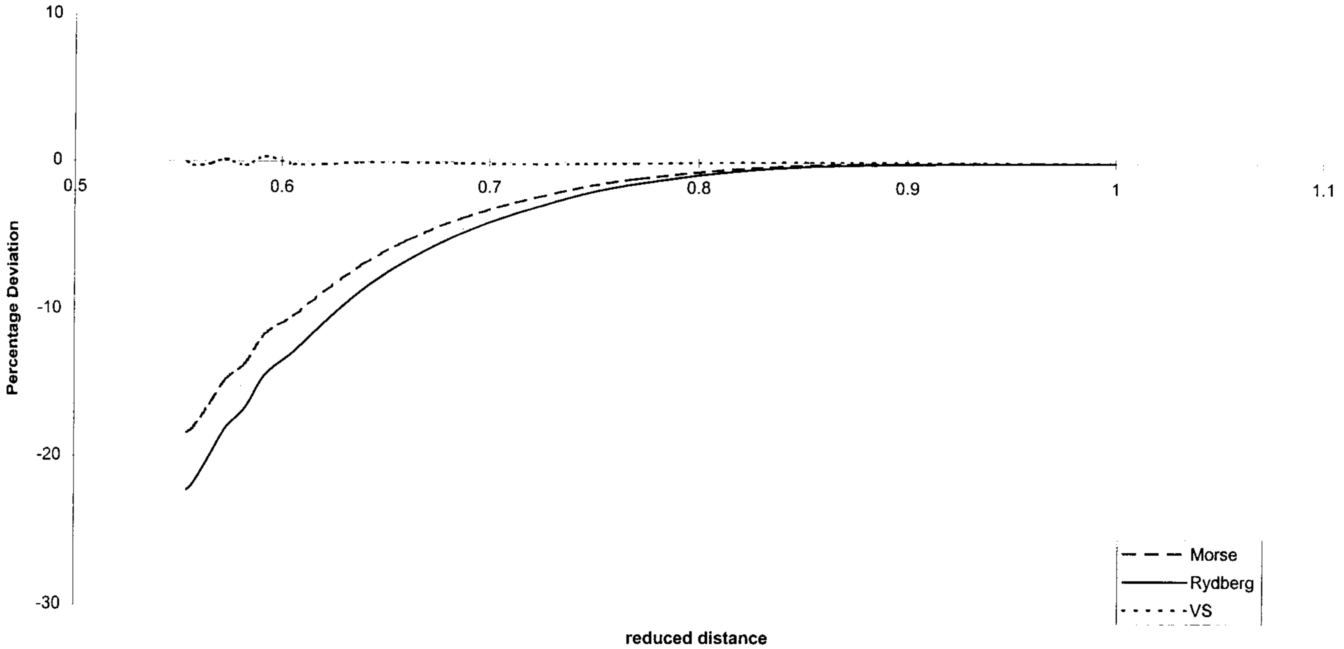

Figure 1. Percentage Deviation of Morse, Rydberg, and VS−PECs from RKR data shown for hydrogen (repulsive branch only). Other homonuclear molecules show similar trend.

TABLE 3: Repulsive Arm ($R \leq R_e$) of the Potential Energy Curve for H_2

reduced distance, R/R_e	RKR[a]/eV	VS/eV	Rydberg/eV	Morse/eV
0.554	4.729	4.680	3.671	3.856
0.557	4.652	4.593	3.613	3.793
0.561	4.522	4.464	3.526	3.670
0.567	4.347	4.298	3.413	3.579
0.573	4.131	4.098	3.275	3.431
0.583	3.88	3.831	3.089	3.232
0.592	3.596	3.579	2.911	3.042
0.606	3.28	3.242	2.669	2.784
0.621	2.936	2.902	2.419	2.519
0.638	2.562	2.538	2.146	2.229
0.660	2.16	2.141	1.840	1.906
0.687	1.73	1.713	1.501	1.549
0.722	1.272	1.257	1.126	1.157
0.770	0.785	0.778	0.716	0.732
0.854	0.269	0.269	0.258	0.261
1.00	0	0	0	0

[a] RKR data obtained from Weissman, S.; Vanderslice, J. T.; Battino, R. *J. Chem. Phys.* **1963**, *87*, 2226.

χ^o is the EN of the neutral VSAs. (ii) The additional on-site electron pair repulsion in a partially filled valence orbital is modeled as $^1/_4 n^2 J$ (with $n = 1-\delta$ being the population of the orbital),[1,2] (iii) $J = I - A$ is the difference between the valence orbital ionization energy I and the corresponding electron affinity A. (iv) The promotion may involve the energy for isovalent or interconfigurational hybridization E_{hyb}; the promotion energy to the barycenter of the spin−orbit split states is included in E_{hyb}. (v) The promotion energies are summed over all bonding valence orbitals for multiple bonds.[2]

For single-bonded polar diatoms we find the VS promotion energy, i.e., the difference between the energy sum of the VS atoms and that of the ground-state atoms, as[3]

$$\sum P^{\delta} = P_X^{+\delta} + P_Y^{-\delta} = P_X^0 + P_Y^0 + E_\chi = \sum E_{hyb} + (1-\delta^2)\sum J/4 \quad (5)$$

The electronegativity equalization energy E_χ is negative

$$E_\chi = -(\chi_x^{o} - \chi_y^{o})^2/(J_x + J_y) \quad (6)$$

TABLE 4: Repulsive Arm ($R \leq R_e$) of the Potential Energy Curve for HF

reduced distance, R/R_e	RKR[a]/eV	VS/eV	Morse/eV	Rydberg/eV
0.678	6.079	5.802	5.217	4.962
0.680	5.992	5.739	5.164	4.913
0.682	5.868	5.626	5.069	4.824
0.685	5.711	5.476	4.943	4.707
0.688	5.527	5.303	4.796	4.570
0.692	5.317	5.108	4.631	4.416
0.697	5.084	4.888	4.444	4.241
0.702	4.830	4.647	4.237	4.049
0.708	4.555	4.388	4.014	3.840
0.715	4.260	4.109	3.773	3.613
0.723	3.947	3.811	3.513	3.369
0.731	3.614	3.495	3.235	3.108
0.741	3.262	3.159	2.939	2.828
0.752	2.892	2.805	2.623	2.530
0.765	2.502	2.431	2.286	2.210
0.781	2.093	2.039	1.930	1.871
0.800	1.664	1.625	1.549	1.506
0.823	1.215	1.190	1.145	1.117
0.856	0.745	0.733	0.712	0.699
0.910	0.254	0.251	0.247	0.245
1.00	0	0	0	0

[a] RKR data from F. Jenč. Private communication.

and reduces the VS promotion energy due to charge transfer.[2] It should be noted, however, that the failure to refer to the appropriate VSs leads to E_χ values amounting to just 50% of those from eq 6;[27] for detailed discussions see refs 1, 2, and 4. For a diatomic molecule, the VS dissociation energy is

$$D_{vs} = D_e + \sum P^{\delta} \quad (7)$$

with D_e the ground-state dissociation energy.

The universal VS function was formulated in accordance with the following asymptotic properties:[2,3] (i) The RHF−PECs of homonuclear diatomics are asymptotically proportional to $1/R$. The VS energies are conceptually related to the RHF model in the homonuclear case. Further arguments for a covalent $1/R$ term have been given by Borkman and Parr[28] and Sanderson.[29] (ii) A $1/R$ attraction is needed for ionic molecules in order to represent the predominance of the Coulombic energy. The

TABLE 5: Repulsive Arm ($R \leq R_e$) of the Potential Energy Curve for LiH

reduced distance, R/R_e	RKR[a]/eV	VS/eV	Morse/eV	Rydberg/eV
0.643	2.253	2.300	2.041	1.943
0.644	2.221	2.290	2.033	1.936
0.646	2.175	2.255	2.004	1.909
0.649	2.119	2.195	1.955	1.863
0.653	2.054	2.119	1.893	1.805
0.658	1.980	2.034	1.822	1.739
0.663	1.899	1.943	1.746	1.668
0.665	1.867	1.910	1.718	1.642
0.672	1.761	1.800	1.626	1.555
0.680	1.650	1.684	1.528	1.464
0.688	1.533	1.564	1.425	1.368
0.698	1.412	1.439	1.318	1.266
0.708	1.285	1.308	1.205	1.159
0.720	1.153	1.173	1.086	1.047
0.733	1.017	1.033	0.962	0.930
0.748	0.875	0.888	0.832	0.806
0.765	0.728	0.738	0.697	0.677
0.786	0.576	0.583	0.555	0.540
0.812	0.418	0.423	0.406	0.397
0.848	0.255	0.258	0.250	0.246
0.906	0.087	0.087	0.086	0.085
1.00	0	0	0	0

[a] RKR data from Vidal, C. R.; Stwalley, W. *J. Chem. Phys.* **1982**, *77*, 883.

TABLE 6: Repulsive Arm ($R \leq R_e$) of the Potential Energy Curve for NaF

reduced distance, R/R_e	RKR[a]/eV	VS/eV	Morse/eV	Rydberg/eV
0.682	6.259	6.525	4.054	3.860
0.709	5.028	4.861	3.188	3.051
0.737	3.661	3.570	2.464	2.370
0.764	2.618	2.574	1.865	1.802
0.791	1.826	1.812	1.375	1.335
0.819	1.238	1.236	0.979	0.955
0.824	1.142	1.140	0.910	0.889
0.832	1.005	1.005	0.813	0.795
0.846	0.804	0.808	0.667	0.653
0.928	0.132	0.134	0.124	0.122
0.996	0	0	0	0

[a] RKR data from F. Jenč. Private communication.

appearance of $1/R$ attractive term is, therefore, a unifying feature in the formulation of a universal VS−PEC. (iii) A screened Coulombic potential, proportional to $(1/R)\exp(-\lambda R)$, is suitable for the repulsive part as it behaves correctly at $R \rightarrow 0$ and may be scaled to fulfill the virial theorem.

The VS−PE function is

$$U(R) = -(C/R) + (T/R)\exp(-\lambda R) \tag{8}$$

The parameters, C, T, and λ, are fitted to R_e, k_e, and $U(\infty) - U(R_e) = D_{vs}$, thence

$$\lambda R_e = k_e R_e^{\,2}/D_{VS} = z \qquad C = D_{VS}R_e(1 + z^{-1}) \qquad \text{and} \qquad T = D_{VS}R_e z^{-1} e^{z} \tag{9}$$

are obtained. The parameter λ is transferable and obeys the arithmetic mean combining rule.[3] In accordance with Coulson and Fischer's results,[23] the VS−PE function is expected to be an effective model for the RKR curves up to $R \leq 1.5R_e$. The advantage of introducing z as the sole species dependent parameter manifests itself in the dimensionless form of the universal VS−PE function:[2]

$$u(s) = \frac{-1 - z + \exp(-zs)}{z(s + 1)} \tag{10}$$

$s = (R - R_e)/R_e$ is the reduced internuclear displacement and $u(s) = U(s)/D_{vs}$, the reduced potential. The derivatives at its minimum, $u(0) = 0$, are

$$u^{(n)}(0) = (-1)^n n! \sum_{i=1}^{n-1} \frac{z^i}{(i + 1)!} \tag{11}$$

for $n \geq 2$.

The most important higher spectroscopic constants, i.e., the vibration−rotation coupling constant α_e and the anharmonicity constant $\tilde{\nu}_e x_e$ with their preferred dimensionless formulations[30] $F = \alpha_e\tilde{\nu}_e/6B_e^{\,2}$ and $G = 8\tilde{\nu}_e x_e/B_e$ are very simple functions of z:

$$F = z/3 \tag{12}$$

$$G = 2z^2/3 + 6z + 3 \tag{13}$$

Varshni and Shukla have tested the related ionic two-parameter PEC (Hellmann PEC) with $C = e^2/4\pi\epsilon_0$ for the alkali metal hydrides.[14] Due to their choice of an ionic scaling factor involving $e^2/4\pi\epsilon_0 R_e$, the expressions for F and G are rather cumbersome for the Hellmann potential.

2.2. Operational Parameters $D_{VS}^{(\alpha)}$ and $z^{(\alpha)}$. While k_e and R_e are experimental values, D_{VS} (and thus z) depends on the amount of hybridization attributed to the VS atoms. The EN and, to a lesser extent, electron repulsion energy J, are functions of the hybridization, therefore the partial charge δ, eq 4 and promotion energy, eq 5, change with hybridization. Similarly, E_{hyb} of the VSA is a direct function of the degree of hybridization. Several analyses of chemical bonding in terms of hybridization[31] and a comparison of the Mulliken and Pauling EN scales[32] have generated rules for estimating the hybridization according to groups in the periodic system. Such rules have been successfully applied to the VS−PEC.[2,3] Nevertheless, each given molecule may demand a detailed investigation because additional factors can have a bearing on D_{VS}. These are primarily the spin−orbit interaction, the inert-pair and other relativistic effects in molecules formed by heavy atoms. The importance of these effects on D_{VS} and the shape of the PEC can be checked by an operational procedure intrinsic to the VS−PEC ansatz. The combination of eqs 9 and 12 and the expression of z in terms of B_e, $\tilde{\nu}_e$, and α_e shows

$$z = \frac{k_e R_e^2}{D_{VS}} = \frac{hc\tilde{\nu}_e^2}{2B_e D_{VS}} = \frac{\alpha_e\tilde{\nu}_e}{2B_e^2} \tag{14}$$

which allows us to introduce an operational definition for the VS dissociation energy[3]

$$\frac{D_{VS}^{(\alpha)}}{hc} = \frac{B_e\tilde{\nu}_e}{\alpha_e} \tag{15}$$

Thus, the spectroscopic constants, B_e, $\tilde{\nu}_e$, and α_e representing the first, second, and third derivatives of U at R_e operationally determine the entire three parameter VS−PEC of any diatom. Nalewajski[15c] and later Tellinghuisen[11,17] took a similar approach to the Morse and Rydberg functions, denoted as [R_e, k_e, α_e] functions. Such reparametrizations have been helpful, since some of the dissociation energies for diatoms are not known with the desired degree of accuracy. Frequently, the D_e values are extrapolated from Birge−Sponer plots, calculated or at worst not known to any appreciable accuracy. Fortunately, α_e has become available for many more molecules and even to a higher accuracy than the anharmonicity constant $\tilde{\nu}_e x_e$.[33,34] The previous concerns of overcongestion of rotational levels in heavy

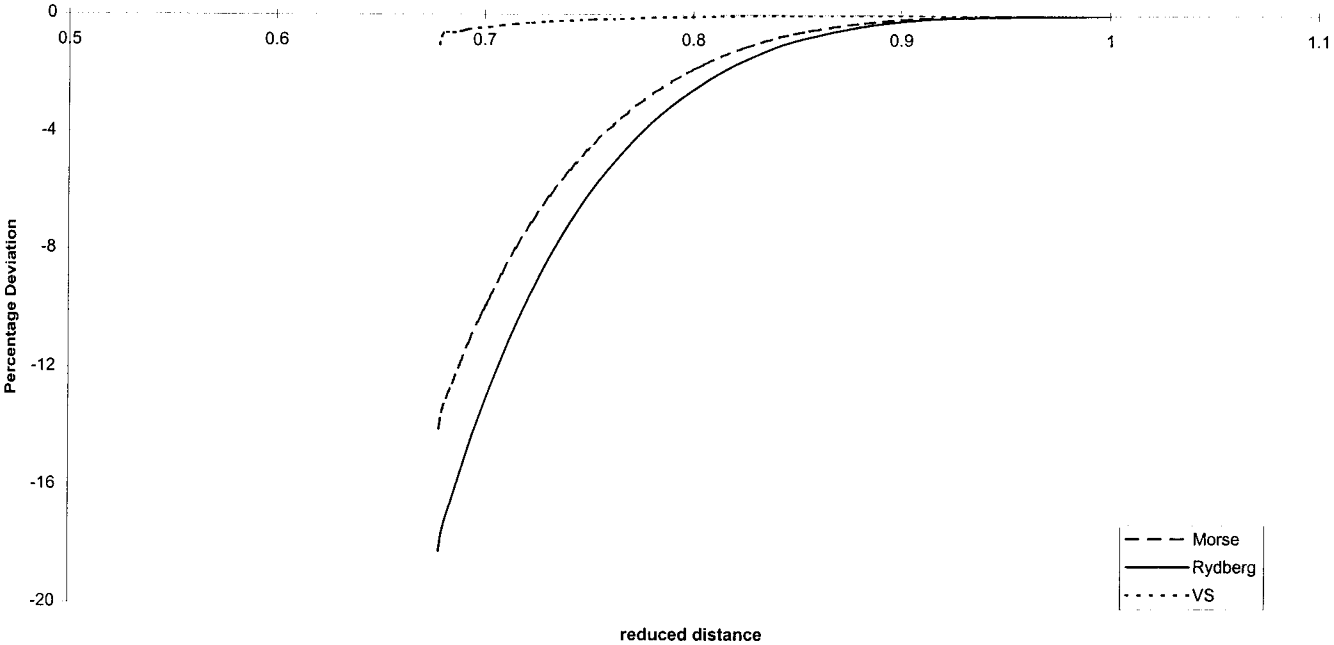

Figure 2. Percentage Deviation of Morse, Rydberg and VS−PECs from RKR data shown for HF (repulsive branch only).

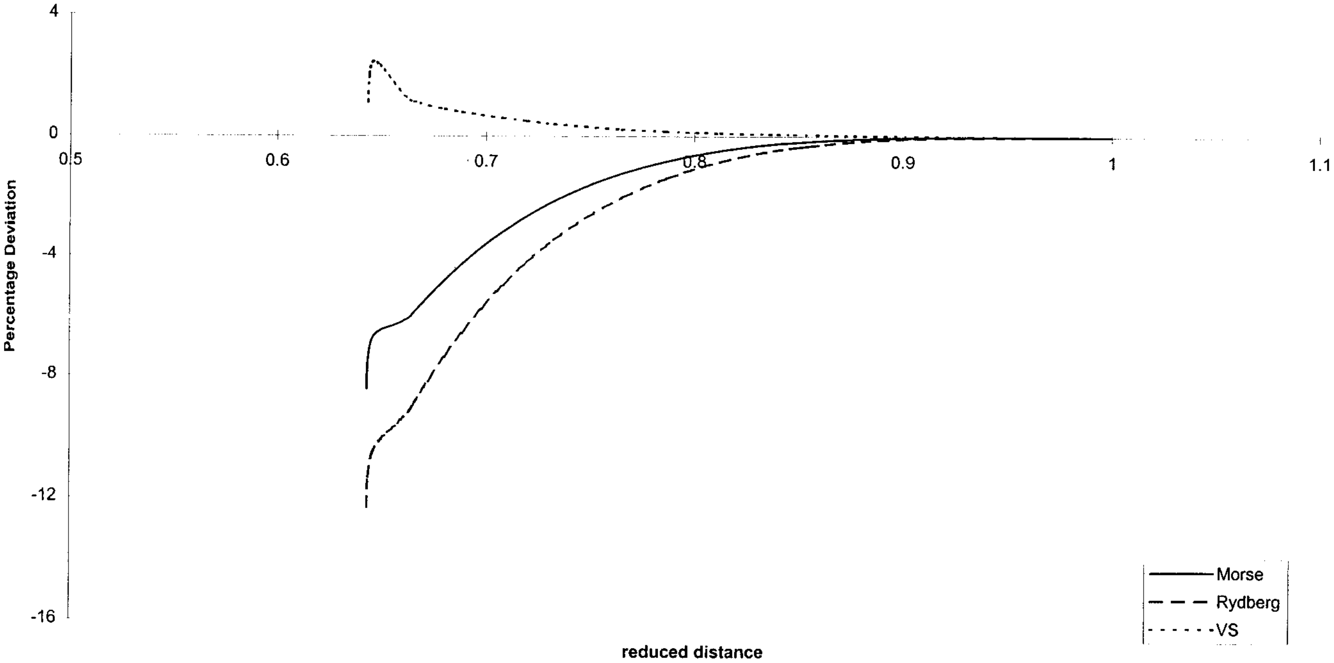

Figure 3. Percentage Deviation of Morse, Rydberg, and VS−PECs from RKR data shown for LiH (repulsive branch only).

molecules are more adequately addressed by the advances in microwave spectroscopic techniques, as documented by the very recent inclusion of tables of diatomic spectroscopic constants in the *1999 Handbook of Chemistry and Physics*.[34]

2.3. Universal Scaling. In general, the reduced PEC is formulated in terms of a dimensionless interatomic displacement q and a scaled potential energy $u(q)$. Postulating also a "reduced" curvature at the minimum, i.e., a universal dimensionless force constant κ, the variable q and $u(q)$ may be defined in terms of a parameter R_{ij}, characterizing the bond between the atoms i and j.[19,20,35] Jenč has discussed several classes of reduced potentials.[20] In the simpler case, first proposed by Frost and Musulin, FM,[35] the parameter R_{ij} is introduced only into the formula for q

$$q = \frac{R - R_{ij}}{R_e - R_{ij}} \tag{16}$$

with

$$R_{ij} = R_e - \left[\frac{\kappa D_e}{k_e}\right]^{1/2}$$

By postulating $R_{ij} = 0$ for H_2 and H_2^+, FM obtained $\kappa = 4.00$ and

$$q_{FM} = \left(\frac{k_e}{4.00 D_e}\right)^{1/2}(R - R_e) + 1 \tag{17}$$

This may be compared to the reduced interatomic displacement

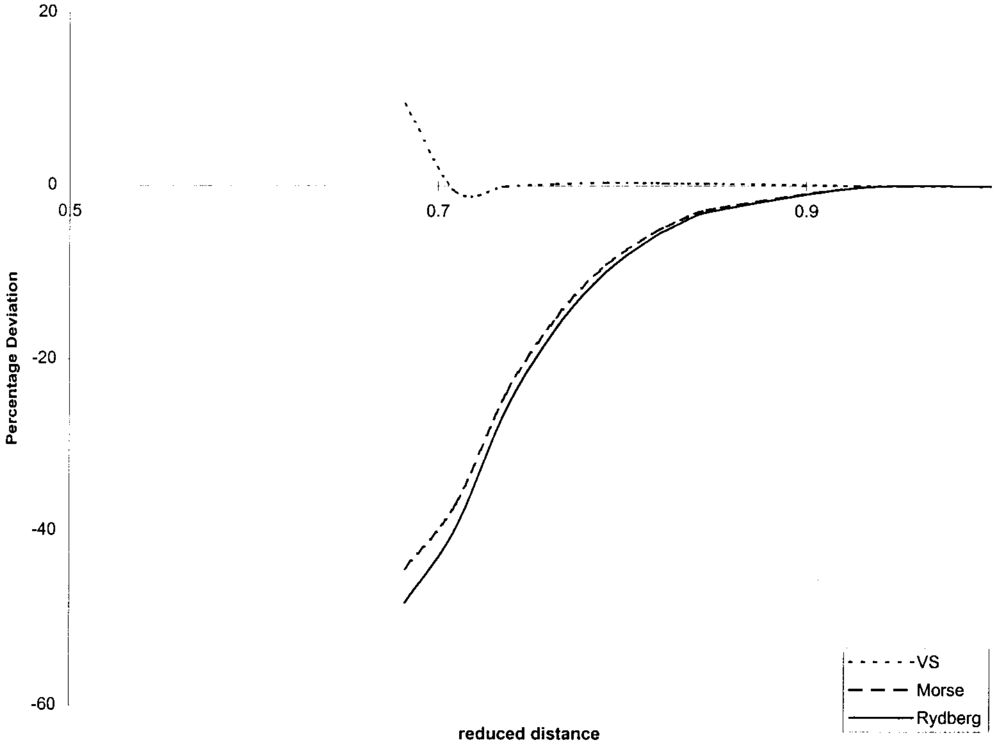

Figure 4. Percentage Deviation of Morse, Rydberg, and VS−PECs from RKR data shown for the ionic NaF (repulsive branch only).

q_M appropriate for the Morse curve:[16,17,21,36]

$$q_M = (k_e/2D_e)^{1/2}(R - R_e) = \Delta^{1/2}s \qquad (18)$$

and the definition of a scaling length l for the Rydberg PEC:[37]

$$q_R = \frac{(R - R_e)}{l} = (k_e/D_e)^{1/2}(R - R_e) = (2\Delta)^{1/2}s \qquad (19)$$

Here, $\Delta = k_e R_e^2/2D_e$ is the Sutherland parameter; for s, see eq 10.

For the VS−PE function, we formulate the displacement factor q_{VS} and the scaled energy U/D_{VS} in order to elicit the reduction of fifty RKR curves into a single universal plot in the Coulson−Fischer range, $0.5R_e < R \leq 1.5R_e$.

$$q_{VS} = z^{1/2}s = (k_e/D_{VS})^{1/2}(R - R_e) \qquad (20)$$

By shifting the reference energy from the VS dissociation limit to $u(0) = 0$, the universal PE function becomes

$$u(q) = \frac{U(q) + D_{VS}}{D_{VS}} = \frac{qp + \exp(-qp) - 1}{qp + p^2} \qquad (21)$$

where $p = z^{1/2}$. The VS subscript has been dropped from q for simplicity.

As pointed out by Jenč,[20] the definitions of q for the various curves differ only in the arbitrarily chosen value of κ and/or the value of q at the minimum of $u(q)$. Notably, the VS displacement q_{VS} differs by the depth of the potential well, i.e., D_{VS} instead of D_e. The comparison with the reduced Morse and Rydberg curves is made using the scaled variables U/D_e and $\Delta^{1/2}$s.

3. Results and Discussion

The hypothesis that "ground state potential energy states for neutral, bound diatomic molecules are universal scaled versions of one another" has been critically examined and found to be of limited applicability by Graves and Parr.[36] The degree to which scaling can be made universal is reexamined for the VS−PEC using the RKR data of 50 molecules, including covalent, partially ionic and ionic diatoms (Table 1). The VS dissociation energies have been calculated by eq 7 and are compared with D_e in Table 1. Their corresponding partial charges in the range $0 \leq \delta < 0.9$, the bond lengths, and harmonic force constants are also listed.

3.1. Operational Dissociation Energies and Self−Consistency of the VS−PEC. The ratios of operational VS dissociation energy and calculated VS dissociation energy $D_{VS}^{(\alpha)}/D_{VS}$ are reported in Table 2 along with $D_{VS}^{(\alpha)}$ and the α_e or F values used in eqs 14 and 15.

The $D_{VS}^{(\alpha)}/D_{VS}$ ratio averages 1.04 for the VS function, a deviation of only 4% from the "perfect ratio". Systematic positive deviations of about 20% from the ideal ratio occur with the five alkali metal dimers, Li_2 to Cs_2. The bonding in these diatoms A_2 is most untypical: (i) the "two-electron bond" is weaker than the "one-electron bond" in the corresponding molecular ion[38] A_2^+ and (ii) the first excited singlet state $A^1\Sigma_u^+$ dissociation energy is larger than that of the $X^1\Sigma_g^+$ ground state. In fact, the spectroscopic constants k_e, B_e, α_e, and D_e, are the same for the ground-state cation and the excited-state neutral diatom.[38,39] For all other molecules, the ratio averages to 1.02 and deviations of the individual molecules are generally small and of random type; they exceed 20% only on 3 of 45 instances. Therefore, we find a good agreement between the theoretically significant D_{VS} and its operational counterpart calculated by eq 15. This observation opens a new and apparently reliable way of predicting dissociation energy D_e, from equilibrium spectroscopic constants. Since the promotion energy ΣP^δ is readily calculable, D_e is obtained by inserting $D_{VS}^{(\alpha)}$ into eq 7:

$$D_e = D_{VS}^{(\alpha)} - \Sigma P^\delta \qquad (22)$$

Earlier studies by Nalewajski[15c] and Tellinghuisen[17] have shown that neither the reparametrized Morse nor Nalewajski's virialized Morse, Rydberg, and Rosen−Morse functions could accomplish the task of successfully calculating D_e from other properties. Like the VS−PEC, the Morse and Rydberg potentials may be fitted to α_e to give operational dissociation energies[11,15c] $D_e^{(\alpha)}$ which are, however, not close to D_e and lack physical meaning. In other words, the VS PEC shows a self-consistency which is absent from the reparametrized $[R_e,k_e,\alpha_e]$ Morse and Rydberg potentials. The ratio $D_e^{(\alpha)}/D_e$ averages 1.34 for Morse and 1.30 for Rydberg. Similar values of 34 and 29% have been obtained for deviation of α_e and $\tilde{\nu}_e x_e$ by Varshni[30a] and similar averages for $D_e^{(\alpha)}/D_e$ by Nalewajski[15c] and Tellinghuisen,[17] though for much smaller sets of bonds. The deviations are systematic: with the exception of H_2, Br_2, I_2, NO, SiS and the ionic molecules, all $D_e^{(\alpha)}/D_e$ ratios are above 1. This is concurrent with the trends observed by Varshni and Tellinghuisen in their evaluations of the Morse potential. However, the systematic deviation $D_e^{(\alpha)} < D_e$, in ionic molecules found for the Morse and Rydberg functions, has not been examined by those authors.

The introduction of the operational parameters to the Morse and Rydberg functions has a further disadvantage. Because $D_e^{(\alpha)}$ is very different from D_e, RKR curves cannot be reduced into a single curve using Morse and Rydberg scaling parameters except if D_e is maintained as the potential well depth. Hence, the reparametrized $[R_e,k_e,\alpha_e]$ Morse and Rydberg functions lose their scaling property.

3.2. Deviation of VS PEC from Rydberg−Klein−Rees (RKR) Curve. The operational VSPE function is compared to original Morse and Rydberg functions through average unsigned deviations.

$$\delta U = \frac{\sum |U_{\mathrm{vs}}(R) - U_{\mathrm{RKR}}(R)|}{nD_e} \tag{23}$$

The most sterling case of impressive VS−PEC performance is H_2 where the average deviation of the VS curve is just over 0.1% whereas those of the Morse and Rydberg curves are approximately 10%. This is evident from Figure 1, which compares the three PECs for the hydrogen diatom. The potential energies, including RKR data,[40] are given in Table 3.

The operational VS−PEC of the partially ionic and ionic molecules, HF, LiH, and NaF also out performs the respective Morse and Rydberg functions as shown in Tables 4−6, respectively. The deviation plots are depicted in Figures 2−4.[41] For the four molecules shown, the deviations of the Morse and Rydberg curves are systematically negative (Figures 2−4). As in section 3.1 above, the VS deviations are small and of random type. The ripples toward the end of the curves at small s are due to slight inaccuracies in the RKR data.[16,42] The complete set of deviations δU, for 50 molecules, are recorded in Table 7. The average unsigned deviation, δU of the VS−PEC for 50 molecules including metal halides and oxides is 1.14%. The deviation of the Morse and Rydberg functions are 3.60 and 3.32%, respectively.

The deviations of the VS function exceed those of the Morse and Rydberg functions only for the higher alkali hydrides (KH, RbH, and CsH), gallium chloride and silver chloride. However, the RKR data are incomplete and inconclusive for the latter two molecules as documented by their rather small ratio $U_{\max}/D_e \approx 0.1$, cf. Table 7. The shortcomings of the VS−PEC for the higher alkali hydrides are rationalized as follows: the core-valence intershell correlation has been found to affect the spectroscopic constants and the PECs as strongly as, or stronger than, the valence-shell correlation.[43] This type of intershell correlation has been very successfully accounted for by the core-polarization-potential (CPP) ansatz.[39,44] For the highly polar alkali hydrides (A^+H^-), the leading term of the CPP is the classical $-\alpha'(A^+)/2R^{-4}$ polarization energy, where α' is the dipole polarizability volume. It seems that Morse's exponential function more adequately models core polarization than the R^{-1} term in the VS−PE function.

TABLE 7: Comparison of δU for Morse, Rydberg, and VS Potentials

molecule	Morse % δU	Rydberg % δU	VS % δU	$U_{\max}/D_e$
Homonuclear				
H_2	9.32	11.4	0.15	0.933
Li_2	9.29	5.71	3.75	1.0
Na_2	10.2	7.44	2.99	1.0
K_2	21.9	17.5	7.22	1.0
Rb_2	8.58	6.25	3.04	0.84
Cs_2	9.17	7.56	2.94	0.678
C_2	0.36	0.11	0.12	0.343
Si_2	0.23	0.13	0.15	0.124
N_2	1.21	0.21	0.77	0.551
P_2	3.27	2.27	1.70	0.514
O_2	0.54	0.86	0.15	0.707
S_2	0.54	1.30	0.47	0.547
Cl_2	7.43	4.02	2.42	1.0
Br_2	4.62	3.18	1.01	0.642
I_2	14.5	9.53	3.13	1.0
Hydrides				
LiH	3.85	5.91	0.89	0.975
NaH	1.40	3.67	1.49	0.973
KH	0.40	1.54	1.89	0.991
RbH	0.69	0.84	0.75	0.574
CsH	2.89	2.06	4.61	0.994
MgH	9.09	10.8	2.09	0.967
CaH	3.31	2.09	0.05	0.603
CH	0.22	0.43	0.56	0.961
SiH	0.07	0.25	0.01	0.19
NH	0.02	0.60	0.23	0.74
OH	1.51	2.95	0.28	0.753
SH	0.52	0.1	0.07	0.415
HF	6.96	9.18	0.33	0.979
HCl	1.41	3.84	0.56	0.989
AgH	0.37	1.33	0.97	0.76
Same Group Heteronuclear				
LiNa	6.33	3.63	2.86	0.961
ICl	0.22	0.10	0.14	0.26
IBr	4.46	3.84	0.12	0.332
Sulphides and Oxides				
CS	0.05	0.33	0.18	0.288
SiS	0.06	0.21	0.04	0.172
NO	1.79	0.45	1.20	‘
SO	1.05	0.97	0.56	0.463
SeO	0.07	0.19	0.08	0.224
Metal Halides, Oxides and Sulphides				
LiF	8.05	8.72	0.21	0.973
NaF	11.5	12.4	1.28	0.907
NaCl	4.31	4.65	0.92	0.931
BeF	1.78	2.26	0.28	0.385
MgF	0.56	0.66	0.21	0.239
AlF	1.24	1.39	0.04	0.191
GaF	0.57	0.63	0.10	0.104
GaCl	0.18	0.15	0.56	0.093
AgCl	2.21	2.01	2.65	0.157
BeO	0.18	0.27	0.19	0.340
MgO	0.64	0.61	0.61	0.280
PbS	0.72	0.45	0.22	0.237
overall	3.60	3.32	1.14	

For 37 of the remaining 45 molecules, the VS−PEC out performs the Morse and Rydberg functions, while the deviations are about equal for eight molecules. The superior performance of the VS function for ionic molecules has been well docu-

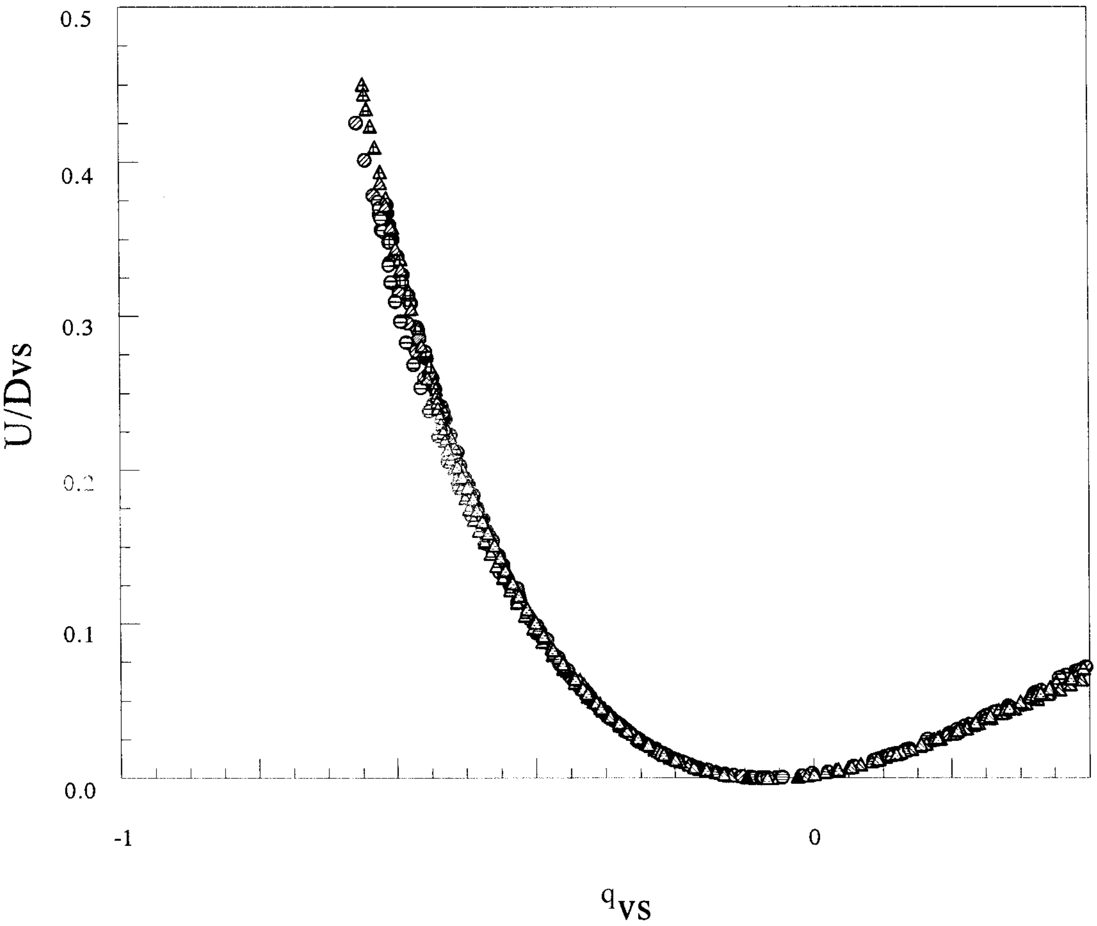

Figure 5. Experimental reduced potential U/D_{VS} plotted against q_{VS} for 50 diatomic molecules (of partial charges between 0 and 0.9) over the Coulson−Fischer range. The curves are so close that they cannot be distinguished.

mented.[2,3] Here, the ionic halides and oxides studied show an average error of 0.4% for VS and over 3% deviation for the Morse and Rydberg curves. We feel that the particular short-range repulsion and the presence of the $1/R$ attraction term, characteristic of ionic molecules equally contribute to this result. We have tested a comprehensive range of molecules and the results discussed reflect the majority of the molecules used. CuH, Al_2, and F_2 have been excluded for the following reasons: For CuH, the s−d mixing ratio changes along the PEC.[45] In Al_2 the rotational structure is highly congested and the ground and first excited electronic states are almost degenerate.[46,47] F_2 has long been known to behave exceptionally due to the effect of the interacting lone pairs, which weaken the bond.[2,3,18−20] Within the group of halogen dimers, the decrease in accuracy for iodine is notable for all three PECs studied (Table 7). The I−I bond in the O_g^+ ground state is weakened by spin−orbit interaction, which is more stabilizing for the separated atoms than for the molecule.[48,49] The distance dependence of spin−orbit coupling influences the spectroscopic constants and the whole RKR curve of heavy p-block dimers and does not seem to be implicitly modeled by any three-parameter PEC.

The introduction of operational Morse and Rydberg parameters results in a significant reduction of the deviation of their inner branch PECs from RKR data.[17] We obtain average absolute deviations of 1.3 and 2.5% (compare 3.60 and 3.32%) for the reparametrized Morse and Rydberg functions, respectively. However, the importance of scaling in comparative studies of the PECs of diatomic molecules has been frequently emphasized[2,3,12,18−20,35−38,50−52] and is presently an active area of research on potential energy curves. We therefore maintain scaling of the Morse and Rydberg curves, at the expense of lower deviations in our comparative study by using the original $[R_e,k_e,D_e]$ Morse and Rydberg functions.

3.3. Universal Reduction within the Coulson−Fischer Range. As pointed out by Frost and Musulin[35] and other authors,[29,30,36] a universal reduced PE function can hardly exist with any precision for all molecules over the whole range of internuclear distances. “There are too many known complexities such as the differing nature of electronic spectroscopic states, or especially the existence of ionic states where the potential energy at large distances would behave quite differently”.[35] The best we can hope for is an approximately reduced PE curve in the neighborhood of the minimum. Figure 5 shows the extent to which the VSAM model allows us to generate a reduced PEC from the experimental RKR data of the 50 ground state diatoms under study. The sample of 50 bonds effectively spans the whole spectrum of polarity from hydrogen to sodium fluoride, corresponding to calculated partial charges $0 \le \delta < 0.9$, cf. Table 1 and eq 1. Using the appropriate scaled coordinates, i.e., $q_{VS} = z^{1/2}s$ with $z = \alpha_e\tilde{\nu}_e/2B_e^2$ and U_{RKR}/D_{VS}, we telescope the PECs of 50 molecules into essentially one curve with a small spread, even in the repulsive region. The range of internuclear distances over which reduction is practically achieved is $R < 1.5R_e$. This is in full agreement with the analysis of Coulson and Fischer[23] and lends support to our modeling the interactions of atoms-in-molecules with reference to their VS dissociation limit.[2−5] In the Coulson−Fischer range of internuclear distances ($R \le 1.5R_e$), the interactions between AIMs can be described by our reduced VS−PEC of eq 21.

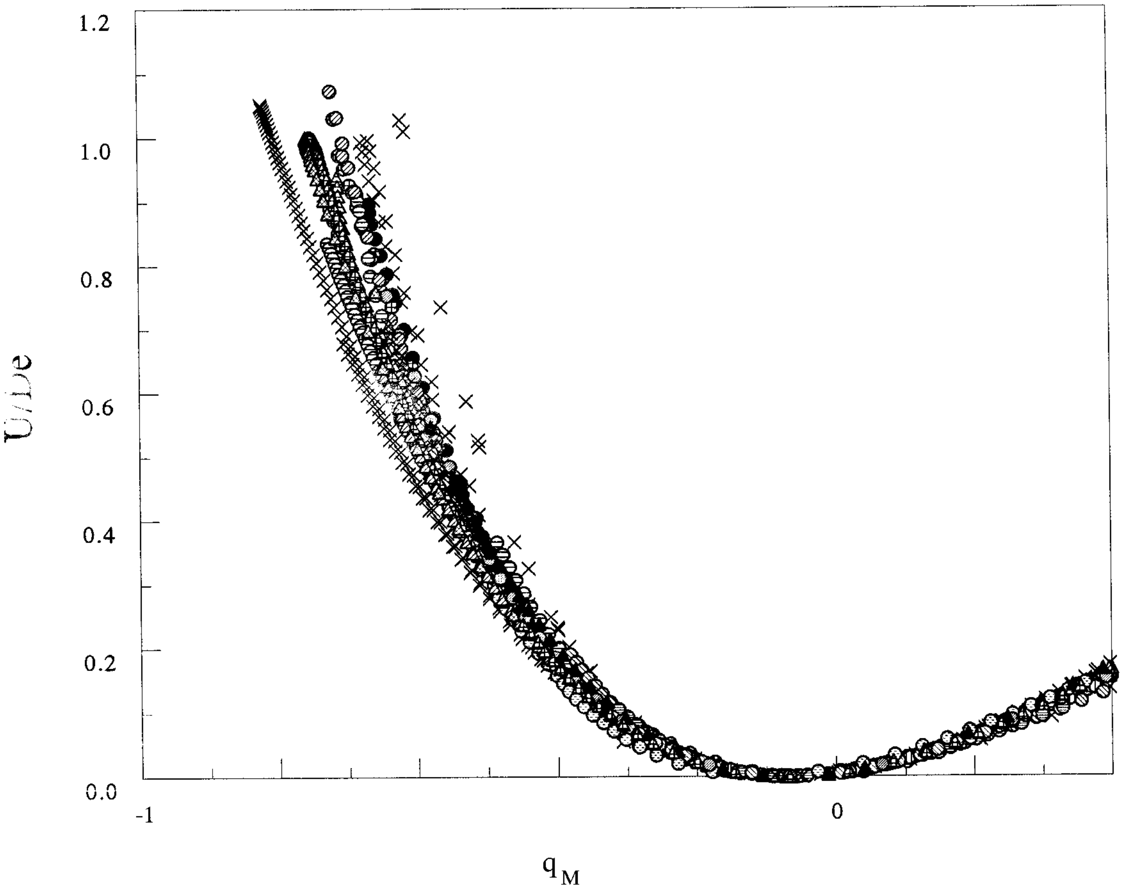

Figure 6. Experimental reduced potential U/D_e plotted against q_M for 50 diatomic molecules (of partial charges between 0 and 0.9) over the Coulson−Fischer range. See text for explanations. The outliers (H_2, Li_2, Na_2, HF, and the metal halides) are represented by X.

Figure 6 shows the reduced PECs obtained from the experimental RKR data of 50 ground state diatoms plotted on Morse type scaled coordinates $\Delta^{1/2}s$ and U/D_e. This coordinate scale is also appropriate for Rydberg scaling since $q_R = 2^{1/2}q_M$, cf. eqs 18 and 19. The overall spread is visibly larger than that in Figure 5. The molecules with largest deviation from the average curve are H_2, Li_2, Na_2 and the highly polar HF and the metal halides, with $\delta > 0.5$. The fact that the Morse and Rydberg scaling parameters cannot universally reduce the RKR curves has been pointed out by Graves and Parr[36] with regard to the relations between Δ and the Dunham coefficients a_1 and a_2. A comparison of the Figures 5 and 6 demonstrates that our scaling with VS parameters is likely to be universally applicable, while those using ground state parameters are not. Remarkably, the spread in the Morse and Rydberg plots increases drastically if the operational parameters $[R_e, k_e, \alpha_e]$ are used, and a bunch of apparently unscaled curves is obtained. The contributing factors are discussed in section 3.1 above.

In order to quantify the scaling achieved in the theoretical range of comparability between the VS−PEC and RKR data, the average absolute deviations, δU have been calculated over the whole Coulson-Fischer range up to $R \leq 1.5R_e$. The deviation of the VS−PEC, averaged over our sample of 50 bonds, increased only slightly from 1.14 to 1.43%. The corresponding values for the Morse and Rydberg curves remain almost constant at 3.60 and 3.45% (compare 3.60 and 3.32%), respectively. The VS−PEC performance remains superior for 35 of 50 molecules, while the Morse and Rydberg perform better for GaCl and AgCl. Reasons for the unreliability of the results for GaCl and AgCl have been given above. Hydrogen and the ionic diatoms are again the molecules for which the best performances are obtained; H_2 shows deviation of 0.13% for VS compared to 7.90 and 9.73% for Morse and Rydberg and the ionic diatoms average 0.54% for seven molecules for the VS function and 2.64 and 2.92% for the Morse and Rydberg functions, respectively. This performance evidences the theoretical soundness of the VSAM model and the VS−PEC. For large distances, the VS−PEC continues upward to its VS dissociation limit and separates from the ground-state RKR curve. A VS hybrid function, developed to model the transition from the VS to ground-state curves, is forthcoming.[53]

4. Conclusion

Generally, the spectroscopic constants, k_e, F, and G, determine the PE function near R_e while the Frost−Musulin criterion[13] highlights the function as R approaches zero. The two regions will be correctly represented only for the exact potential function. The failure of exponential type potential functions (Morse, Rydberg, Rosen−Morse and others) to fulfill this criterion is important with regard to universality. Only the VS,[2,3] Frost-Musulin,[13] and Nalewajski[15c] potentials exhibit proper behavior as R approaches zero; of these, our VS−PEC is the most quantitatively tested. The repulsive branches of diatomic potentials are remarkably simple, permitting a surprisingly reliable prediction from closed-form potentials based on only three equilibrium spectroscopic constants.

Morse and Rydberg PECs do not properly describe the interaction of AIMs. The reduced Morse and Rydberg functions are unable to reproduce the RKR data of a broad range of diatoms. The reduced VS curve matches the RKR data closely. The VS success is not coincidental: (i) Mulliken has long ago pointed out that an appropriate VS dissociation energy is more theoretically significant than D_e.[54] (ii) Recent comparisons of AIM concepts[4,6] show that it is necessary to incorporate Ruedenberg's molecular VS concept[24] into the definitions of EN, hardness, and gas-phase electrophilicity of atoms and groups in molecules.

The reference to the VS energy, appropriate for dissociating AIMs, is crucial for the construction a universal three parameter VS−PEC which describes the in situ covalent and ionic interactions in a unified way. The VS dissociation energy D_{vs} is shown as a parameter with high information content, and $z^{1/2}$ acts as the scaling factor in the universal reduction of the inner branch of VS−PECs. The knowledge of the form of the inner branch can be used to predict the outer branch of the PEC, hence full curves may be obtained by methods discussed earlier.[11,16,17] On the basis of the foregoing results, we conclude that the performance of the Valence State PE function is superior to the others studied.

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