One-Center Integrals of the Exact Effective Valence Shell Hamiltonian. Empirical Analysis for Atoms

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Abstract: The exact effective valence shell Hamiltonian ($\mathcal{H}^v$) which operates within a predetermined valence shell producing exact valence state energies and which can, in principle, be evaluated to arbitrary accuracy by purely systematic ab initio methods is analyzed. Specific application is made to the outer ns–np valence shell of C, N, O, F, Si, P, and S in order to determine the exact one-center integrals of $\mathcal{H}^v$ for comparison with recent ab initio calculations and with semiempirical theories which attempt to mimic $\mathcal{H}^v$. The linearly independent matrix elements of the one-, two-, and three-electron effective interactions of $\mathcal{H}^v$ are obtained and it is shown that three-electron effective interactions are important. Some of these matrix elements are uniquely determined by atomic spectroscopic data. An optimal set of the remaining matrix elements is generated by a least-squares fit. The relationship between the empirical one-center $\mathcal{H}^v$ matrix elements and the one-center, one- and two-electron parameters of semiempirical methods is given elsewhere.

I. Introduction

The concept of orbitals is central to the understanding of the electronic structure of atoms and molecules. Rigorously, one-electron orbitals are no more than convenient mathematical constructs for representing the fully correlated all-electron eigenstates of the electronic Hamiltonian. However, from a more naive standpoint, the orbitals for a given system are often taken to possess a physical significance of their own when used within the context of simple models of bonding. In many cases, ideas based on a simple molecular orbital picture can clearly describe certain chemical phenomena. The orbitals naturally fall into three groups—core, valence, and excited. Within a zeroth-order model of electronic structure, the frozen core orbitals are fully occupied in all the valence states, those states which are important for describing ordinary chemistry; the excited orbitals are vacant; the valence orbitals, being only partially occupied and the major variable of the model, largely control the processes of ordinary chemistry. This simple picture of valence theory is used to explain large blocks of phenomenology like the periodicity of the chemical properties of the elements and general trends in bonding.

A. Semiempirical Theories of Valence. The phenomenological importance of valence electrons coupled with the unwieldiness and expense of accurate ab initio calculations is the basic motivation behind the development of semiempirical valence theories.[2a] Beginning with Hückel theory,[2b] then with Pariser–Parr–Pople theory,[2a,3] semiempirical theories have evolved through myriad variations on the theme.[4] The conceptual impetus of these theories is the postulate that there exists a model Hamiltonian, $\mathcal{H}^v{}_M$, which operates only on a prechosen set of valence electrons which are moving in the field of the frozen core.[4] It is assumed that $\mathcal{H}^v{}_M$ has the general form

$$\mathcal{H}^v{}_M = E_c + \sum_{i=1}^{N_v} \mathcal{H}^v{}_M(i) + 1/2! \sum_{i=1}^{N_v} \sum_{j=1}^{N_v}{}' \mathcal{H}^v{}_M(i,j) \qquad (1)$$

where E_c is the energy of the correlated frozen core, N_v is the number of valence electrons, and $\mathcal{H}^v{}_M(i)$ and $\mathcal{H}^v{}_M(i,j)$ are effective one- and two-body operators respectively. The primed summation indicates that $i = j$ is not allowed. By adjusting the matrix elements of $\mathcal{H}^v{}_M(i)$ and $\mathcal{H}^v{}_M(i,j)$ within the chosen set of valence orbitals, it is hoped that the effects of correlation can be incorporated, so that the spectrum of $\mathcal{H}^v{}_M$ matches the portion of the spectrum of the full Hamiltonian, H, which corresponds to the valence states of interest. The determination of these matrix elements, or parameters, is accomplished with the aid of experimental data and often with ad hoc assumptions based on "chemical intuition". The specific details of the determination of the semiempirical parameters characterize each of the different theories. One of the basic assumptions concerning semiempirical parameters is that they are functions of local environment and, therefore, are transferable among similar systems. One variation, due to Raynor and Hashmall,[5] takes the parameters as functions of the occupation numbers of the orbitals.

The development of semiempirical theories of valence has been marred, in part, by the lack of systematic guiding principles. Given the assumed general form in (1), each investigator introduces his own brand of chemical intuition along with his personal parameterization scheme. This lack of a theoretical foundation and the morass of different semiempirical methods has led some to conclude that these semiempirical approaches are nothing but interpolation methods which proceed in the absence of any systematic knowledge of what the parameterization is or should be doing. In view of the unavailability of rigorous theoretical guides and the utility of semiempirical methods, others have attempted to optimize the semiempirical methods within the uncertain confines of a given parameterization scheme.

The present paper is part of our continuing efforts to provide a fully rigorous, systematic ab initio theoretical basis for the derivation and calculation of the properties of the true effective valence shell Hamiltonian[4,6–11] which is being mimicked by semiempirical model Hamiltonians. The ultimate goal is to provide a solid theoretical connection between improved semiempirical theories of electronic structure and first principles, ab initio theories.

B. Effective Hamiltonian Theories. In an effort to understand the many remarkable successes and occasional disappointing failures of semiempirical theories,[12,13] we have been studying the theory,[6–8] properties, and ab initio calculation[9–11] of the effective valence shell Hamiltonian, $\mathcal{H}^v$, for atomic and molecular systems. $\mathcal{H}^v$ is an operator which is derived (as opposed to postulated in semiempirical theories) from the full electronic Schrödinger equation, yet it depends explicitly only upon valence orbitals. Since $\mathcal{H}^v$ is *exact*, the spectrum of $\mathcal{H}^v$ is *identical* with the portion of the spectrum of H which is associated with the valence states of the atomic or molecular system.

The subspace of the N-electron Hilbert space, within which $\mathcal{H}^v$ is defined, is called the valence space (or P space). Given

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a complete, orthonormal set of one-electron orbitals, $\{\phi\}$, which are partitioned into core $\{\phi_c\}$, valence $\{\phi_v\}$, and excited sets $\{\phi_e\}$

$$\{\phi\} = \{\phi_c\} + \{\phi_v\} + \{\phi_e\} \tag{2}$$

the valence space is spanned by the set of all Slater determinants in which the core orbitals are doubly occupied by the N_c core electrons and the remaining $N_v = N - N_c$ valence electrons are distributed among the valence orbitals in all distinct ways. The excited orbitals are vacant in all valence space configurations. The complement to the valence space (or Q space) is defined by all other N-electron Slater determinants which are characterized by having at least one vacant core orbital (hole) and/or at least one occupied excited orbital (particle).

C. Derivation of $\mathcal{H}^v$. Proof of the existence of $\mathcal{H}^v$ follows directly from partitioning theory by first writing the Schrödinger equation in matrix notation:

$$\mathbf{HC} = E\mathbf{C} \tag{3a}$$

where $\mathbf{C}$ is the column matrix of coefficients in the wave function expansion in terms of the above noted complete set of Slater determinants. Equation 3a is rewritten in block form as

$$\begin{pmatrix} \mathbf{H}_{PP} & \mathbf{H}_{PQ} \\ \mathbf{H}_{QP} & \mathbf{H}_{QQ} \end{pmatrix} \begin{pmatrix} \mathbf{C}_P \\ \mathbf{C}_Q \end{pmatrix} = E \begin{pmatrix} \mathbf{C}_P \\ \mathbf{C}_Q \end{pmatrix} \tag{3b}$$

where $\mathbf{H}_{PP}$ is the subblock of the full Hamiltonian in P space, $\mathbf{H}_{PQ} = \mathbf{H}^+_{QP}$ contains the coupling between P and Q space, $\mathbf{C}_P$ is a vector in P space of P-space configuration coefficients, etc. Equation 3b can be separated into two equations:

$$\mathbf{H}_{PP}\mathbf{C}_P + \mathbf{H}_{PQ}\mathbf{C}_Q = E\mathbf{C}_P \tag{4a}$$

$$\mathbf{H}_{QP}\mathbf{C}_P + \mathbf{H}_{QQ}\mathbf{C}_Q = E\mathbf{C}_Q \tag{4b}$$

Formally solving (4b) for $\mathbf{C}_Q = (E\mathbf{I}_{QQ} - \mathbf{H}_{QQ})^{-1}\mathbf{H}_{QP}\mathbf{C}_P$, and substituting the result into (4a) gives the well-known relation[14]

$$\{\mathbf{H}_{PP} + \mathbf{H}_{PQ}(E\mathbf{I}_{QQ} - \mathbf{H}_{QQ})^{-1}\mathbf{H}_{QP}\}\mathbf{C}_P = E\mathbf{C}_P \tag{5}$$

where $\mathbf{I}_{QQ}$ is the identity matrix in Q space. The inverse matrix $(E\mathbf{I}_{QQ} - \mathbf{H}_{QQ})^{-1}$ is defined solely within Q space and is, in principle, infinite. Since the bracketed term in (5) is a matrix defined only on the valence space with eigenvalues E which are a subset of the eigenvalues of the original Schrödinger equation (3), we draw the obvious conclusion that the bracketed term is one representation[6-8,15-19] of the effective valence shell Hamiltonian matrix.

$$\mathcal{H}^v = \mathbf{H}_{PP} + \mathbf{H}_{PQ}(E\mathbf{I}_{QQ} - \mathbf{H}_{QQ})^{-1}\mathbf{H}_{QP} \tag{6}$$

The conclusion is obvious since there is a one-to-one correspondence between the configurations appearing in the full treatment of the semiempirical, model Schrödinger equation, $\mathcal{H}^v{}_M\mathbf{C}_P = E\mathbf{C}_P$, and those appearing in the exact effective valence shell Schrödinger equation (5).

D. Properties of $\mathcal{H}^v$. Having demonstrated the existence of $\mathcal{H}^v$, which is the object being modeled in semiempirical theories by $\mathcal{H}^v{}_M$, we turn to examine the structure of the individual matrix elements of $\mathcal{H}^v$. From the form of eq 6, it can be shown that $\mathcal{H}^v$ has nonzero matrix elements between valence space determinants which differ by *more* than two electrons. This is a direct consequence of treating the degrees of freedom associated with $\mathbf{C}_Q$ in (4b) implicitly through $\mathbf{H}_{PQ}(E\mathbf{I}_{QQ} - \mathbf{H}_{QQ})^{-1}\mathbf{H}_{QP}$ rather than explicitly as in eq 3. In other words, it is generally true that in operator language $\mathcal{H}^v$ consists not only of one- and two-electron operators, as postulated by semiempirical $\mathcal{H}^v{}_M$'s (see eq 1), but also three-, four-, . . . , up to N_v-electron effective valence shell operators.

$$\mathcal{H}^v = E_c + \sum_{i=1}^{N_v} \mathcal{H}^v{}_1(i) + 1/2! \sum_{i=1}^{N_v} \sum_{j=1}^{N_v}{}' \mathcal{H}^v{}_{12}(i,j) + 1/3! \sum_{i=1}^{N_v} \sum_{j=1}^{N_v}{}' \sum_{k=1}^{N_v}{}'' \mathcal{H}^v{}_{123}(i,j,k) + \ldots \tag{7}$$

The presence of these nonclassical many-electron effective operators, $\mathcal{H}^v{}_{123}, \ldots$, is the price that must be paid in order to have a valence shell Hamiltonian that is exact!

Since *all* valence space configurations have a fully occupied core and a vacant excited space, the effects of core-core, core-valence, core-excited, valence-excited, and excited-excited correlation must be included in the effective operators, $E_c, \mathcal{H}^v{}_1, \mathcal{H}^v{}_{12}, \ldots, \mathcal{H}^v{}_{12\ldots N_v}$. The valence-valence correlation is incorporated by diagonalizing $\mathcal{H}^v$ within the valence space. This is analogous to a full valence configuration interaction calculation.

Based on the diagrammatic quasi-degenerate many-body perturbation formulation of Brandow,[16] and the second quantized, generalized perturbation theory of Freed[20] as applied to effective valence shell Hamiltonian theory by Iwata and Freed,[7] we have recently shown how very general ab initio perturbative formulas may be derived for the individual valence integrals of the operators, $\mathcal{H}^v{}_1, \ldots, \mathcal{H}^v{}_{12\ldots N_v}$.[8] As the derivations employ a Rayleigh-Schrödinger-type formulation, the state energies, E, in (6) are likewise expanded in a perturbation series, so the resultant expressions for the matrix elements of $\mathcal{H}^v$ are energy independent. Discussions of the pros and cons of various formalisms can be found elsewhere.[4,6-11] The approximate evaluation of these formulas can also be related through the partitioning formalism to the B_k method of Gershgorn and Shavitt[21] and the configuration selection method of Segal and Wetmore.[22] The latter methods are now standard approximate ab inito configuration approaches. The valence integrals of the effective valence shell Hamiltonian within this formalism are shown to satisfy the following criteria:

(1) The integrals of $\mathcal{H}^v$ are independent of the valence state energy.

(2) The integrals of $\mathcal{H}^v$ are independent of the number of valence electrons in the system; they depend, in part, upon the choice of valence orbitals.

(3) The integrals can be evaluated independently, thus allowing the separation of the matrix elements of $\mathcal{H}^v$ into individual 0, 1, 2, . . . , N_v-electron contributions, which take the form of integrals of $\mathcal{H}^v{}_1, \ldots, \mathcal{H}^v{}_{12\ldots N_v}$ between particular valence shell spin orbitals.

(4) A very general form of perturbation theory, involving matrix energy denominators which incorporate a valence orbital dependence, may be used without destroying criteria (1)-(3).

Criteria (1)-(3) are important to facilitate comparison with semiempirical theories whereas criterion (4) is important to ensure convergence of the ab initio formulas in certain pathological cases, for example, when large core polarization effects are important as in the π Hamiltonian of ethylene,[9] or when so called "intruder" states or low-lying Rydberg states are present (see discussion in section III).

E. Fundamental Questions Concerning the Structure of $\mathcal{H}^v$. Of particular interest to us are the integrals of the individual effective operations, $\mathcal{H}^v{}_1, \mathcal{H}^v{}_{12}, \ldots, \mathcal{H}^v{}_{12\ldots N_v}$. Because of their close relationship to the parameters of semiempirical theories, we refer to them as true parameters. The answers to several questions concerning the true parameters are important both for understanding and developing a solid theoretical basis for improved semiempirical theories and for checking approximation schemes for evaluating $\mathcal{H}^v$. This is necessary in order to develop the effective valence shell Hamiltonian into an accurate ab initio method which can add to our understanding of electronic structure. Some of the questions to be answered are as follows:

(a) How large are contributions from "nonclassical" three-, four-, . . . , and higher-electron true parameters, especially since they are absent in semiempirical theories?

(b) How do the true parameters depend upon the particular choice of valence orbitals?

(c) What information can be obtained from experimental data concerning the true parameters, and how can it be used as an aid in understanding both semiempirical and ab initio theories?

(d) How are the effects of three- and higher-electron true parameters averaged into one- and two-electron semiempirical parameters? And is this averaging done in a consistent manner?

(e) How good are the major assumptions of semiempirical theories such as neglect of differential overlap (NDO) and the hypothesis of transferability? Some of the more evolved semiempirical theories, like MINDO and MNDO, rely less on the NDO approximation than do the earlier ones.

Partial answers to questions (a) and (b) have been obtained through second-order calculations of $\mathcal{H}^{\mathrm{v}}$ for first- and second-(long) row atoms.[10,11] It is shown in these papers that three-electron true parameters can make contributions of the order of several electronvolts to excitation energies and ionization potentials. Questions (d) and (e) have also been partially investigated.[23,24]

In the following sections, question (c) is studied in detail and is used to analyze (a) and (b) from an empirical point of view. Implications for ab initio calculations are also discussed. Further investigation of questions (d) and (e) is left for future papers.

Section II briefly introduces the notation for the relationships between the true parameters, while in section III empirical values for the true one-center parameters are deduced from atomic spectral data. Section IV provides a discussion of the results. Ab initio calculations of $\mathcal{H}^{\mathrm{v}}$ matrix elements and the comparison between the empirical and ab initio $\mathcal{H}^{\mathrm{v}}$ matrix elements and one-center semiempirical integrals are discussed elsewhere.[10,11]

II. True Parameters

The definitions of the true parameters are obtained as spatial integrals of the effective one-, two-, three-, . . . , N_{v}-electron operators between valence orbitals.

$$\begin{aligned}
\langle v|v'\rangle &= \int \mathrm{d}r\phi_v{}^*(\mathbf{r})\ \mathcal{H}^{\mathrm{v}}{}_1(r)\ \phi_{v'}(r)\\
\langle vw|v'w'\rangle &= \iint \mathrm{d}\mathbf{r}_1\ \mathrm{d}\mathbf{r}_2\ \phi^*{}_v(\mathbf{r}_1)\ \phi^*{}_w(\mathbf{r}_2)\\
&\qquad \times \mathcal{H}^{\mathrm{v}}{}_{12}(\mathbf{r}_1,\mathbf{r}_2)\ \phi_{v'}(\mathbf{r}_1)\ \phi_{w'}(\mathbf{r}_2)\\
\langle uvw|u'v'w'\rangle &= \iint \mathrm{d}\mathbf{r}_1\ \mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{r}_3\ \phi^*{}_u(\mathbf{r}_1)\phi^*{}_v(\mathbf{r}_2)\phi^*{}_w(\mathbf{r}_3)\\
&\qquad \times \mathcal{H}^{\mathrm{v}}{}_{123}\,(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)[\phi_{u'}(\mathbf{r}_1)\phi_{v'}(\mathbf{r}_2)\phi_{w'}(\mathbf{r}_3)\\
&\qquad - \phi_{w'}(\mathbf{r}_1)\phi_{v'}(\mathbf{r}_2)\ \phi_{u'}(\mathbf{r}_3)] \qquad (8)\\
&\qquad \vdots
\end{aligned}$$

Spin integrations can easily be appended to the one- and two-electron true parameters; however, for the three-electron true parameters, spin cannot be included in such a trivial way.

Since electrons can have only two different values of spin (α or β), and since the Pauli principle leads to exchange contributions when two electrons have the same spin, any physically meaningful quantity that requires three-electron integrals must require them at least in pairs; i.e., three-electron integrals can never appear independently because at least two out of three electrons must have the same spin, thus generating exchange contributions. Therefore, the three-electron true parameters, which are matrix elements of the three-body interactions in $\mathcal{H}^{\mathrm{v}}$, are defined as linear combinations of two three-electron spin-independent integrals as in (8). This introduces no problems since all matrix elements of $\mathcal{H}^{\mathrm{v}}{}_{123}$ can be expressed in terms of the three-electron true parameters; for example, a little algebra generates

$$\begin{aligned}
&\Big\langle \phi_u(1)\alpha(1)\phi_v(2)\alpha(2)\phi_w(3)\alpha(3)\\
&\qquad \times \left| \frac{1}{3!} \sum_{i=1}^{3} \sum_{j=1}^{3}{}' \sum_{k=1}^{3}{}'' \mathcal{H}^{\mathrm{v}}{}_{123}(i,j,k) \right|\\
&\qquad \times \phi_{u'}(1)\alpha(1)\phi_{v'}(2)\alpha(2)\phi_{w'}(3)\alpha(3)\Big\rangle = \langle uvw|u'v'w'\rangle\\
&\qquad\qquad - \langle uvw|v'u'w'\rangle - \langle uvw|u'w'v'\rangle \qquad (9)
\end{aligned}$$

where $|\phi_u(1)\sigma_u(1)\ \ldots\ \phi_{u'}(N_{\mathrm{v}})\sigma_{u'}(N_{\mathrm{v}})\rangle$ represents a normalized Slater determinant of valence orbitals. Since $\mathcal{H}^{\mathrm{v}}$ does not affect core orbitals, and since all valence space basis states have a full core, the core may implicitly be assumed to be present.

In a similar manner, the four-electron true parameters are defined as linear combinations of four four-electron spin independent integrals.

III. Empirical Analysis for Atoms

As an example of the kinds of information which can be obtained from experimental data concerning the true parameters, we consider the empirical analysis of $\mathcal{H}^{\mathrm{v}}$ for first- and second-row atoms. In these systems we choose to label the outer shell s, p_x, p_y, and p_z orbitals as valence in accord with simple pictures of valence. (In the second row, the 3d orbitals could be appended to the valence shell if desired.)

The spatial symmetry of the valence orbitals, the Hermitian property of $\mathcal{H}^{\mathrm{v}}$, and the indistinguishability of electrons are used to generate the list of spin-free, nonzero, independent, zero-, one-, two-, and three-electron true parameters appearing in Table I. An important symmetry difference between the true parameters and the ordinary two-electron repulsion integrals is the fact that $\langle vw|wv\rangle$ and $\langle vv|ww\rangle$ are not necessarily equal even if $\{\phi_{\mathrm{v}}\}$ were chosen to be real. For example, $\langle sx|xs\rangle$ and $\langle ss|xx\rangle$ are listed as distinct true parameters in Table I. Again, this result is a direct consequence of the explicit formulas for the *exact* $\mathcal{H}^{\mathrm{v}}$.

To obtain empirical relations between the true parameters, the 17 valence state energies for $N_{\mathrm{v}} = 0$, 1, 2, and 3, expressed in terms of the zero-, one-, two-, and three-electron true parameters, are set equal to their experimental values. Three additional empirical relations are obtained by using the fact that valence states with the same total orbital angular momentum (and number of electrons) but diffferent projections along a specified axis must have the same energy. As a result, we are able to establish 20 empirical relations among the 22 true parameters. (See Appendix I for the equations.)

The empirical energies[25-27] are obtained by performing a degeneracy weighted average $(2J + 1)$ over the multiplet splittings for each term.[27] Corrections are made to compensate for the fact that the value of the Rydberg constant is different for each atom. No attempt is made to correct for the small relativistic effects. Their main contribution is to the core energy, E_{c}.

Starting with the zero valence electron ^{1}S state (eq I.1) and working up, it is found that 12 of the 22 true parameters can be uniquely determined empirically. These true parameters are marked with footnote *a*, Table I. The remaining ten true parameters are related by eight empirical equations, thereby allowing the elimination of all but two true parameters; $\langle ss|ss\rangle$ and $\langle ssx|ssx\rangle$ are chosen as our two independent variables for convenience.

The fact that 12 of the true parameters have unique empirical values implies that for any ab initio theory in which the true parameters can be separately evaluated and satisfy criteria

Table I. True Parameters of $\mathcal{H}^{\mathrm{v}}$ (eV)

	C	N	O	F	Si	P	S[b]
E_{c}[a]	−882.12	−1219.15	−1610.77	−2057.11	−7784.83	−9128.32	−10 582.04
$\langle s\|s\rangle$[a]	−64.50	−97.89	−138.12	−185.19	−45.14	−65.03	−88.05
$\langle x\|x\rangle$[a]	−56.49	−87.90	−126.13	−171.19	−36.27	−53.97	−74.82
$\langle ss\|ss\rangle$	17.47	21.04	24.61	28.24	11.97	14.28	
$\langle sx\|sx\rangle$[a]	18.20	22.69	27.16	31.63	11.20	13.36	15.19
$\langle sx\|xs\rangle$[a]	3.10	3.93	4.72	5.56	1.85	2.28	2.71
$\langle ss\|xx\rangle$	2.48	2.43	2.16	1.73	1.42	2.20	
$\langle xx\|xx\rangle$	19.93	25.56	31.15	36.72	10.23	13.11	
$\langle xy\|xy\rangle$[a]	18.17	23.02	27.86	32.66	9.53	12.10	13.34
$\langle xy\|yx\rangle$[a]	0.52	0.82	1.10	1.41	−0.48	0.05	−0.41
$\langle xx\|yy\rangle$	1.23	1.72	2.19	2.65	1.18	0.97	
$\langle ssx\|ssx\rangle$	−1.90	−1.55	−1.19	−0.87	−0.40	−0.97	
$\langle sxx\|sxx\rangle$	−2.33	−2.37	−2.53	−2.64	−0.33	−0.82	
$\langle sxx\|syy\rangle$	−0.34	−0.48	−0.64	−0.80	−0.30	0.07	
$\langle sxy\|sxy\rangle$[a]	−1.87	−1.95	−1.97	−1.90	−0.43	−0.87	0.21
$\langle sxy\|syx\rangle$[a]	−0.12	0.06	0.08	0.06	0.40	−0.02	0.51
$\langle sxy\|xsy\rangle$[a]	0.06	−0.27	−0.21	−0.23	−0.16	−0.13	−0.14
$\langle xyz\|xyz\rangle$[a]	−2.97	−2.85	−2.87	−2.79	1.01	−2.13	
$\langle xyz\|xzy\rangle$[a]	−0.17	−0.15	−0.12	−0.13	0.99	−0.56	
$\langle xyy\|xss\rangle$	−1.54	−1.53	−1.14	−0.95	0.69	−0.60	
$\langle xyy\|xyy\rangle$	−3.28	−3.05	−3.11	−3.09	1.10	−2.37	
$\langle xyy\|xzz\rangle$	−0.14	−0.05	−0.12	−0.17	−0.90	0.32	

[a] Uniquely determined true parameters. [b] Empirical energies for $N_{\mathrm{v}} = 2$ and 3 are not all available, specifically ^{1}S(3p^2) and ^{2}D$^{\mathrm{o}}$(3p^3).

(1) and (2) of section 1, these 12 true parameters should be *independent* of the mathematical form chosen for the valence *orbitals* provided that the ab initio calculations of $\mathcal{H}^{\mathrm{v}}$ have included all the contributing terms. Thus a good test of convergence for the ab initio theory involves a comparison of the ab initio and empirical values of these unique true parameters. The comparison can be used in two different ways. (1) Since the true parameters are independent of the valence space in an exact calculation, the numerical approximations of the particular calculational scheme, such as using a finite basis and truncating the perturbation expansion, can be tested by comparing the parameters from several different choices of valence orbitals. (2) A scheme for choosing a good set of valence orbitals can be determined by testing convergence as a function of valence orbitals. These two tests have already been used in our recent ab initio calculations of $\mathcal{H}^{\mathrm{v}}$ for first- and second-row atoms through second order in perturbation theory.[10,11] Third-order calculations are in progress.[28]

From an ab initio point of view, the remaining ten nonunique true parameters must be functions of the mathematical form chosen for the valence orbitals. The functions themselves are arbitrary and are, of course, unknown empirically. By using the Hermitian property of $\mathcal{H}^{\mathrm{v}}$, which requires all energies to be real, it is possible to obtain upper and lower bounds for the two free variables, $\langle ss|ss\rangle$ and $\langle ssx|ssx\rangle$.

$$E[{}^1S(s^2)] \le \langle ss|ss\rangle + 2\langle s|s\rangle + E_{\mathrm{c}} \le E[{}^1S(p^2)] \qquad (10a)$$

$$\begin{aligned} E[{}^2\mathrm{P}^{\mathrm{o}}(s^2p)] \le {} & \langle ssx|ssx\rangle + \langle ss|ss\rangle \\ & + 2\langle sx|sx\rangle - \langle sx|xs\rangle \\ & + 2\langle s|s\rangle + \langle x|x\rangle + E_{\mathrm{c}} \le E[{}^2\mathrm{P}^{\mathrm{o}}(p^3)] \end{aligned} \qquad (10b)$$

(Equations 10 are easily derived from Appendix I.) The allowed region for $\langle ss|ss\rangle$ and $\langle ssx|ssx\rangle$ is pictured in Figure 1.

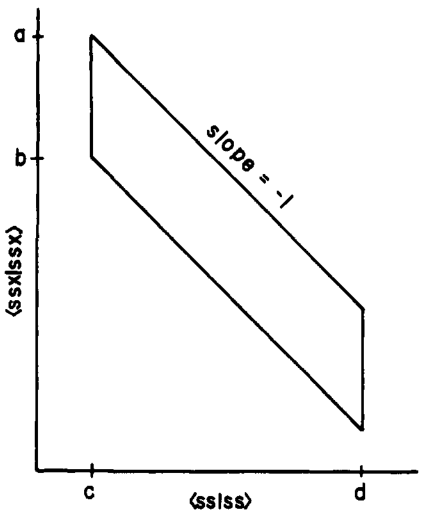

Figure 1. Allowed region for true parameters is interior to the parallelogram where $a = E[{}^2\mathrm{P}^{\mathrm{o}}(p^3)] - \langle ss|ss\rangle - 2\langle sx|sx\rangle + \langle sx|xs\rangle - 2\langle s|s\rangle - \langle x|x\rangle - E_{\mathrm{c}}$, $b = E[{}^2\mathrm{P}^{\mathrm{o}}(s^2p)] - \langle ss|ss\rangle - 2\langle sx|sx\rangle + \langle sx|xs\rangle - 2\langle s|s\rangle - \langle x|x\rangle - E_{\mathrm{c}}$, $c = E[{}^1\mathrm{S}(s^2)] - 2\langle s|s\rangle - E_{\mathrm{c}}$, and $d = E[{}^1\mathrm{S}(p^2)] - 2\langle s|s\rangle - E_{\mathrm{c}}$.

So far in the analysis we have neglected the existence of four- and higher-electron true parameters which we, and certainly all semiempirical chemists, would like to believe is a reasonable approximation. However, by pursuing the analysis further it is possible to get an estimate of the cumulative magnitude of these effective many-electron effects in the best cases. To do this, the valence state energies for $N_{\mathrm{v}} = 4$, 5, 6, and 7 are expressed in terms of the zero-, one-, two-, and three-electron true parameters (see Appendix II). Using the two-dimensional freedom of the nonunique true parameters, we are able to minimize the contributions of the omitted four- and higher-electron effects in a nonlinear least-squares sense. Specifically, we minimize the function $f(\langle ss|ss\rangle, \langle ssx|ssx\rangle)$ given by

$$f(\langle ss|ss\rangle, \langle ssx|ssx\rangle) = \sum_i (E^0{}_i - E_i(\langle ss|ss\rangle, \langle ssx|ssx\rangle))^2 \qquad (11)$$

where $E^0{}_i$ is the empirical value of the valence state energy, E_i is the corresponding energy expression from Appendix II, and i is summed over all known (to us) energy states with N_{v} greater than or equal to 4. The residuals, $E^0{}_i - E_i$, at the minimum are reported in Table II, and the corresponding set of true parameters, both unique and nonunique, is reported in Table I for each atom.

The function f seems to be trough shaped on the parallelogram of Figure 1, with the bottom of the ditch starting near the point (c,b) and traversing the region in a nearly straight

Table II.[a] Least-Square Residuals after Minimizing Four- and Higher-Body Effects (See Equation 11)

state designation	configuration	C	N	O	F	Si	P
^1S	p^4			−0.29	−0.16		
^1D	p^4			−0.02	−0.02		
^3P	p^4			−0.07	−0.07		
$^1P^o$	sp^3		−0.03	−0.18	+0.03		−0.01
$^3S^o$	sp^3		−0.30	−0.08	−0.09	−0.52	+0.01
$^1D^o$	sp^3		−0.45	−0.23	−0.15		−0.40
$^3P^o$	sp^3	−0.35	−0.37	+0.00	+0.05	−1.46	+0.80
$^3D^o$	sp^3	−0.23	−0.09	+0.08	+0.01	−2.91	+2.10
$^5S^o$	sp^3	−0.11	−0.10	+0.20	−0.02	−0.15	+0.08
^1S	s^2p^2	+0.06	+0.07	+0.14	+0.26	+0.27	−0.29
^1D	s^2p^2	+0.24	+0.15	+0.01	−0.12	−0.39	+1.31
^3P	s^2p^2	−0.47	+0.15	+0.06	−0.13	−0.45	+0.23
$^2P^o$	p^5				−0.44		
^2P	sp^4			−0.70	−0.54		−0.57
^2S	sp^4			−0.42	+0.02		+0.96
^2D	sp^4			−0.19	−0.19		+5.79
^4P	sp^4		−0.74	+0.11	−0.12		+4.06
$^2P^o$	s^2p^3		−0.10	+0.04	−0.14		+1.63
$^2D^o$	s^2p^3		−0.22	−0.18	−0.62		+3.54
$^4S^o$	s^2p^3		−0.25	−0.04	−0.65		+0.45
^1S	p^6						
$^1P^o$	sp^5			−0.36	−0.67		
$^3P^o$	sp^5			−0.44	−0.63		
^1S	s^2p^4			−0.11	−0.18		
^1D	s^2p^4			−0.87	−1.36		
^3P	s^2p^4			−0.75	−1.40		
^2S	sp^6				−2.15		
$^2P^o$	s^2p^5				−2.95		

[a] Energies for $N_v = 0, 1, 2, 3$ which are used to determine the true parameters in Table I are exactly reproduced, i.e., $(E^o{}_i - E_i) \equiv 0$ for $N_v = 0, 1, 2, 3$.

line of approximate slope zero. The bottom of the ditch is relatively flat over long distances and has at least two local minima, both of which give reasonable values for the true parameters $\langle ss|ss\rangle$ and $\langle ssx|ssx\rangle$ and nearly identical values for f. We attach no significance to the fact that in all cases reported the local minimum closest to the point (c,b) proved to be slightly superior for minimizing f.

It should be emphasized that this scheme is not the only way to fix the remaining degrees of freedom. However, it does give insight into the importance of the effective many-electron effects which is part of our purpose. From Table II, it can be seen that these effects are generally on the order of tenths of an electronvolt except for a few states. The effects are also generally larger for second-row atoms, indicating that the polarizability of the core may be one of the important factors for estimating the magnitude of the contributions of the many-electron true parameters.

It is probably not safe to search Table II for states with large errors and then conclude that effective many-electron effects are most important only for these states. The reason for this lies in the nonuniqueness of the chosen form of $f(\langle ss|ss\rangle, \langle ssx|ssx\rangle)$ in eq 11. For instance, we could have chosen to minimize the errors in excitation energies and ionization potentials due to the omission of many-electron true parameters rather than errors in absolute energies. The result would have been to shift the errors associated with each state, thus possibly changing the pairing between large errors and certain states.

Finally, there is the possibility that some of the experimental energies could be misassigned, especially for second-row atoms where intruder states and low-lying Rydberg states mix strongly with valence states. Silicon provides a good example in which there is a large discrepancy between certain ab initio[11] and their corresponding unique empirical true parameters. The discrepancy can be traced to the sign of the energy splitting between the $^2D^o(3p^3)$ valence state and the $^2D^o(3s3p3d)$ "intruder" excited state of Si^+. The ab initio second-order calculation seems to be converging to the lower level which is empirically assigned to $^2D^o(3s3p3d)$. This type of problem is typical of any energy-independent (Rayleigh–Schrödinger type) perturbation theory when intruder states are present.[29]

IV. Conclusions

The effective valence shell Hamiltonian is discussed from an empirical standpoint, both as an ab initio electronic structure method and as the theoretical foundation of improved semiempirical theories. We demonstrate, within a formalism in which the true parameters are independent of the charge on the atom and also of the valence state energy, that certain of the true parameters must be independent of the chosen form of the valence orbitals in ab initio calculations. These empirically determined unique true parameters can serve as a measure of convergence for ab initio calculations of $\mathcal{H}^v$. The remaining true parameters are empirically nonunique and, therefore, must be functions of the form of the valence orbitals chosen in ab initio calculations. By using the two degrees of freedom among the nonunique true parameters, we show that the total contribution from four- and higher-electron true parameters may be important for certain valence states, but is in general only on the order of a few tenths of an electronvolt for the atoms studied.

In spite of the nonuniqueness associated with eq 11, there are several general trends which we believe are valid and important. First, the overall magnitude of the many-electron true parameters is accurately represented by the numbers in Table II. The fact that the errors are larger for larger N_v is reasonable since the weight with which the many-electron true parameters enter in the energy expressions increases significantly with increasing N_v. Also, the errors are larger for second-row atoms than for first-row atoms. This is probably due, in part, to the existence of low-lying "intruder" states which involve the 3d orbitals and mix strongly with valence states. In order to compensate for this strong mixing between P and Q space, large contributions are required from the many-electron true parameters. One solution to this problem is to include 3d orbitals in the valence shell; however, this remedy is not without its own maladies, i.e., an enlarged valence space, more complicated formulas, more true parameters to evaluate, insufficient experimental data, etc.

Another trend which is apparent from Table I is that, except for E_c, the true parameters decrease in magnitude from the first to the second row. This is a consequence of the fact that excitation energies and ionization potentials are smaller for second-row atoms since the ($1s^2 2s^2 2p^6$) core is softer, allowing for more core reorganization, and the valence electrons, being further from the nucleus in the second-row atoms, can be further from each other. In silicon and sulfur, the true parameter, $\langle xy|yx\rangle$, actually changes sign due to the inversion of the ^{1}D(p^2) and ^{3}P(p^2) levels in Si^{2+} and S^{4+}.

The ramifications of the fact that certain four-electron true parameters may also be uniquely determined have not been considered here, but will be analyzed in detail in conjunction with third-order ab initio calculations of $\mathcal{H}^v$. Four-electron true parameters first appear in the third-order theory.[28]

In relation to semiempirical theories, the one- and two-electron semiempirical parameters have quite different values than the one- and two-electron true parameters.[10,11] This suggests that some averaging of effective many-electron effects has been incorporated in semiempirical parameters at the expense of transferability between states of the same atom involving different charge and/or local electronic structure. A preliminary study of this averaging has already been reported elsewhere by Freed and Sun.[23]

It should be pointed out that the high symmetry associated with the atomic valence space plays an important role in allowing the unique determination of so many of the true parameters. For molecules, the situation is much worse since the number of true parameters increases much faster than the number of valence state energies. In CH, for example, where the valence orbitals are chosen to be the 2σ, 3σ, $1\pi_x$, $1\pi_y$, and 4σ molecular orbitals, only the $\langle 1\pi_x|1\pi_x\rangle = \langle 1\pi_y|1\pi_y\rangle$ true one-electron parameter can, in principle, be uniquely determined. The remaining six one-electron true parameters ($\langle 2\sigma|2\sigma\rangle$, $\langle 3\sigma|2\sigma\rangle$, $\langle 3\sigma|3\sigma\rangle$, $\langle 4\sigma|2\sigma\rangle$, $\langle 4\sigma|3\sigma\rangle$, and $\langle 4\sigma|4\sigma\rangle$) are related by only three empirical equations, but these are not readily measured experimentally since to our knowledge CH^{4+} is not known. The situation gets much worse as symmetry is reduced and the atomic numbers increase. Consequently, there is a great need for both theory and calculations before $\mathcal{H}^v$ is completely understood in molecular systems.

Finally, it should also be emphasized that the empirical one-center true parameters cannot necessarily be transferred to molecules as is customarily assumed in semiempirical theories of valence. As there is unsufficient experimental data for molecules to rigorously test the transferability hypothesis empirically, this important question is to be resolved by ab initio calculations of $\mathcal{H}^v$ for molecular systems. The empirical analysis of the present paper provides an important check on these ab initio methods for atomic systems as a prelude to the molecular calculations. General theoretical considerations show that the true parameters are molecule dependent, and preliminary calculations on CH, NH, and OH do indicate the presence of some nonnegligible changes even in the one-center two-electron true parameters in going from the atom to the molecule. (The calculated molecular one-center one-electron true parameters have first-order contributions due to the field of the other atomic centers, making a comparison between atomic and molecular values difficult.)

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Appendix I. Energy Expressions and Relations between True Parameters for N_v = 0, 1, 2, and 3

$$N_v = 0$$

$$E[^1\mathrm{S}] = E_c \tag{1.1}$$

$$N_v = 1$$

$$E[^2\mathrm{P^o(p)}] = E_c + \langle x|x\rangle \tag{1.2}$$

$$E[^2\mathrm{S(s)}] = E_c + \langle s|s\rangle \tag{1.3}$$

$$N_v = 2$$

$$E[^1\mathrm{D(p^2)}] = E_c + 2\langle x|x\rangle + \langle xy|xy\rangle + \langle xy|yx\rangle \tag{1.4}$$

$$E[^3\mathrm{P(p^2)}] = E_c + 2\langle x|x\rangle + \langle xy|xy\rangle - \langle xy|yx\rangle \tag{1.5}$$

$$E[^1\mathrm{P^o(sp)}] = E_c + \langle s|s\rangle + \langle x|x\rangle + \langle sx|sx\rangle + \langle sx|xs\rangle \tag{1.6}$$

$$E[^3\mathrm{P^o(sp)}] = E_c + \langle s|s\rangle + \langle x|x\rangle + \langle sx|sx\rangle - \langle sx|xs\rangle \tag{1.7}$$

$$\left.\begin{array}{l} E[^1\mathrm{S(p^2)}] \\ E[^1\mathrm{S(s^2)}] \end{array}\right]\begin{array}{l} + \\ - \end{array} = E_c + \langle s|s\rangle + \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + \tfrac{1}{2}\langle xx|xx\rangle + \langle xx|yy\rangle \pm [(\langle s|s\rangle - \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle - \tfrac{1}{2}\langle xx|xx\rangle - \langle xx|yy\rangle)^2 + 3\langle ss|xx\rangle^2]^{1/2} \tag{1.8}$$

$$\langle xy|xy\rangle + \langle xy|yx\rangle = \langle xx|xx\rangle - \langle xx|yy\rangle \tag{1.9}$$

$$N_v = 3$$

$$E[^2\mathrm{D^o(p^3)}] = E_c + 3\langle x|x\rangle + 3\langle xy|xy\rangle + \langle xyz|xyz\rangle + \langle xyz|xzy\rangle \tag{1.10}$$

$$E[^4\mathrm{S^o(p^3)}] = E_c + 3\langle x|x\rangle + 3\langle xy|xy\rangle - 3\langle xy|yx\rangle + \langle xyz|xyz\rangle - 2\langle xyz|xzy\rangle \tag{1.11}$$

$$E[^2\mathrm{P(sp^2)}] = E_c + \langle s|s\rangle + 2\langle x|x\rangle + 2\langle sx|sx\rangle + \langle sx|xs\rangle + \langle xy|xy\rangle - \langle xy|yx\rangle + \langle sxy|sxy\rangle - \langle sxy|syx\rangle + 2\langle sxy|xsy\rangle \tag{1.12}$$

$$E[^2\mathrm{S(sp^2)}] = E_c + \langle s|s\rangle + 2\langle x|x\rangle + 2\langle sx|sx\rangle - \langle sx|xs\rangle + \langle xx|xx\rangle + 2\langle xx|yy\rangle + \langle sxx|sxx\rangle + 2\langle sxx|syy\rangle \tag{1.13}$$

$$E[^2\mathrm{D(sp^2)}] = E_c + \langle s|s\rangle + 2\langle x|x\rangle + 2\langle sx|sx\rangle - \langle sx|xs\rangle + \langle xy|xy\rangle + \langle xy|yx\rangle + \langle sxy|sxy\rangle + \langle sxy|syx\rangle \tag{1.14}$$

$$E[^4\mathrm{P(sp^2)}] = E_c + \langle s|s\rangle + 2\langle x|x\rangle + 2\langle sx|sx\rangle - 2\langle sx|xs\rangle + \langle xy|xy\rangle - \langle xy|yx\rangle + \langle sxy|sxy\rangle - \langle sxy|xsy\rangle - \langle sxy|syx\rangle \tag{1.15}$$

$$\left.\begin{array}{l} E[^2\mathrm{P^o(p^3)}] \\ E[^2\mathrm{P^o(s^2p)}] \end{array}\right]\begin{array}{l} + \\ - \end{array} = E_c + \langle s|s\rangle + 2\langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + \langle sx|sx\rangle - \tfrac{1}{2}\langle sx|xs\rangle + \tfrac{1}{2}\langle xx|xx\rangle + \langle xy|xy\rangle - \tfrac{1}{2}\langle xy|yx\rangle + \tfrac{1}{2}\langle xx|yy\rangle + \tfrac{1}{2}\langle ssx|ssx\rangle + \tfrac{1}{2}\langle xyy|xyy\rangle + \tfrac{1}{2}\langle xyy|xzz\rangle \pm [(\langle s|s\rangle - \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + \langle sx|sx\rangle - \tfrac{1}{2}\langle sx|xs\rangle - \tfrac{1}{2}\langle xx|xx\rangle - \langle xy|xy\rangle + \tfrac{1}{2}\langle xy|yx\rangle - \tfrac{1}{2}\langle xx|yy\rangle + \tfrac{1}{2}\langle ssx|ssx\rangle - \tfrac{1}{2}\langle xyy|xyy\rangle - \tfrac{1}{2}\langle xyy|xzz\rangle)^2 + 2(\langle ss|xx\rangle + \langle xyy|xss\rangle)^2]^{1/2} \tag{1.16}$$

$$\begin{aligned}&\langle xyz|xyz\rangle + \langle xyz|xzy\rangle \\ &\qquad = \langle xyy|xyy\rangle - \langle xyy|xzz\rangle \qquad (I.17)\end{aligned}$$

$$\begin{aligned}&\langle sxy|sxy\rangle + \langle sxy|syx\rangle \\ &\qquad = \langle sxx|sxx\rangle - \langle sxx|syy\rangle \qquad (I.18)\end{aligned}$$

Appendix II. Energy Expressions for N_v = 4, 5, 6, 7 Omitting Four- and Higher-Electron True Parameters

$$N_v = 4$$

$$\begin{aligned}E[{}^1\mathrm{P^o(sp^3)}] = {}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + 3\langle sx|sx\rangle \\ & + 3\langle xy|xy\rangle + 2\langle xx|yy\rangle + 2\langle sxy|sxy\rangle \\ & - \langle sxy|syx\rangle + 3\langle sxy|xsy\rangle + \langle sxx|sxx\rangle \\ & + \langle xyy|xyy\rangle + \langle xyy|xzz\rangle + \langle sxx|syy\rangle \qquad (II.1)\end{aligned}$$

$$\begin{aligned}E[{}^3\mathrm{S^o(sp^3)}] = {}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + 3\langle sx|sx\rangle \\ & + \langle sx|xs\rangle + 3\langle xy|xy\rangle - 3\langle xy|yx\rangle + 3\langle sxy|sxy\rangle \\ & - 3\langle sxy|syx\rangle + 5\langle sxy|xsy\rangle + \langle xyz|xyz\rangle \\ & - 2\langle xyz|xzy\rangle \qquad (II.2)\end{aligned}$$

$$\begin{aligned}E[{}^1\mathrm{D^o(sp^3)}] = {}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + 3\langle sx|sx\rangle \\ & + 3\langle xy|xy\rangle + 3\langle sxy|sxy\rangle + 3\langle sxy|xsy\rangle \\ & + \langle xyy|xyy\rangle - \langle xyy|xzz\rangle \qquad (II.3)\end{aligned}$$

$$\begin{aligned}E[{}^3\mathrm{P^o(sp^3)}] = {}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + 3\langle sx|sx\rangle \\ & - 2\langle sx|xs\rangle + 2\langle xy|xy\rangle - \langle xy|yx\rangle + \langle xx|xx\rangle \\ & + \langle xx|yy\rangle + \langle sxx|sxx\rangle + 2\langle sxy|sxy\rangle - \langle sxy|syx\rangle \\ & - \langle sxy|xsy\rangle + \langle xyy|xyy\rangle + \langle sxx|syy\rangle \\ & + \langle xyy|xzz\rangle \qquad (II.4)\end{aligned}$$

$$\begin{aligned}E[{}^3\mathrm{D^o(sp^3)}] = {}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + 3\langle sx|sx\rangle \\ & - 2\langle sx|xs\rangle + 3\langle xy|xy\rangle + 3\langle sxy|sxy\rangle \\ & - \langle sxy|xsy\rangle + \langle xyy|xyy\rangle - \langle xyy|xzz\rangle \qquad (II.5)\end{aligned}$$

$$\begin{aligned}E[{}^5\mathrm{S^o(sp^3)}] = {}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + 3\langle sx|sx\rangle \\ & - 3\langle sx|xs\rangle + 3\langle xy|xy\rangle - 3\langle xy|yx\rangle \\ & + 3\langle sxy|sxy\rangle - 3\langle sxy|syx\rangle - 3\langle sxy|xsy\rangle \\ & + \langle xyz|xyz\rangle - 2\langle xyz|xzy\rangle \qquad (II.6)\end{aligned}$$

$$\left.\begin{matrix}E[{}^1\mathrm{S(p^4)}] \\ E[{}^1\mathrm{S(s^2p^2)}]\end{matrix}\right]\begin{matrix}+\\-\end{matrix} =$$

$$\begin{aligned}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 2\langle sx|sx\rangle \\ & - \langle sx|xs\rangle + \tfrac{3}{2}\langle xx|xx\rangle + 2\langle xy|xy\rangle - \langle xy|yx\rangle \\ & + 2\langle xx|yy\rangle + \langle ssx|ssx\rangle + \langle sxx|sxx\rangle \\ & + 2\langle sxx|syy\rangle + 2\langle xyy|xyy\rangle + 2\langle xyy|xzz\rangle \\ & \pm [(\langle s|s\rangle - \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 2\langle sx|sx\rangle \\ & - \langle sx|xs\rangle - \tfrac{1}{2}\langle xx|xx\rangle - 2\langle xy|xy\rangle + \langle xy|yx\rangle \\ & + \langle ssx|ssx\rangle + \langle sxx|sxx\rangle + 2\langle sxx|syy\rangle - 2\langle xyy|xyy\rangle \\ & - 2\langle xyy|xzz\rangle)^2 + 4(\langle ss|xx\rangle + 2\langle xyy|xss\rangle)^2]^{1/2} \qquad (II.7)\end{aligned}$$

$$\left.\begin{matrix}E[{}^1\mathrm{D(p^4)}] \\ E[{}^1\mathrm{D(s^2p^2)}]\end{matrix}\right]\begin{matrix}+\\-\end{matrix} =$$

$$\begin{aligned}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 2\langle sx|sx\rangle \\ & - \langle sx|xs\rangle + \tfrac{1}{2}\langle xx|xx\rangle + 3\langle xy|xy\rangle + \langle ssx|ssx\rangle \\ & + \langle sxy|sxy\rangle + \langle sxy|syx\rangle + \langle xyy|xyy\rangle + \langle xyz|xyz\rangle \\ & + \langle xyz|xzy\rangle \pm [(\langle s|s\rangle - \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle \\ & + 2\langle sx|sx\rangle - \langle sx|xs\rangle - \tfrac{1}{2}\langle xx|xx\rangle - 2\langle xy|xy\rangle \\ & + \langle xy|yx\rangle + \langle ssx|ssx\rangle + \langle sxy|sxy\rangle + \langle sxy|syx\rangle \\ & - \langle xyy|xyy\rangle - \langle xyz|xyz\rangle - \langle xyz|xzy\rangle)^2 \\ & + (\langle ss|xx\rangle + 2\langle xyy|xss\rangle)^2]^{1/2} \qquad (II.8)\end{aligned}$$

$$\left.\begin{matrix}E[{}^3\mathrm{P(p^4)}] \\ E[{}^3\mathrm{P(s^2p^2)}]\end{matrix}\right]\begin{matrix}+\\-\end{matrix} =$$

$$\begin{aligned}& E_c + \langle s|s\rangle + 3\langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 2\langle sx|sx\rangle \\ & - \langle sx|xs\rangle + \tfrac{1}{2}\langle xx|xx\rangle + 3\langle xy|xy\rangle - 2\langle xy|yx\rangle \\ & + \langle ssx|ssx\rangle + \langle sxy|sxy\rangle - \langle sxy|syx\rangle \\ & + \langle xyy|xyy\rangle + \langle xyz|xyz\rangle \\ & - \langle xyz|xzy\rangle \pm [(\langle s|s\rangle - \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle \\ & + 2\langle sx|sx\rangle - \langle sx|xs\rangle - \tfrac{1}{2}\langle xx|xx\rangle - 2\langle xy|xy\rangle \\ & + \langle xy|yx\rangle + \langle ssx|ssx\rangle + \langle sxy|sxy\rangle - \langle sxy|syx\rangle \\ & - \langle xyy|xyy\rangle - \langle xyz|xyz\rangle + \langle xyz|xzy\rangle)^2 \\ & + (\langle ss|xx\rangle + 2\langle xyy|xss\rangle)^2]^{1/2} \qquad (II.9)\end{aligned}$$

$$N_v = 5$$

$$\begin{aligned}E[{}^2\mathrm{P(sp^4)}] = {}& E_c + \langle s|s\rangle + 4\langle x|x\rangle + 4\langle sx|sx\rangle \\ & + \langle xx|xx\rangle + 5\langle xy|xy\rangle - 3\langle xy|yx\rangle + \langle sxx|sxx\rangle \\ & + 5\langle sxy|sxy\rangle - 3\langle sxy|syx\rangle + 6\langle sxy|xsy\rangle \\ & + 2\langle xyy|xyy\rangle + 2\langle xyz|xyz\rangle - 2\langle xyz|xzy\rangle \qquad (II.10)\end{aligned}$$

$$\begin{aligned}E[{}^2\mathrm{S(sp^4)}] = {}& E_c + \langle s|s\rangle + 4\langle x|x\rangle + 4\langle sx|sx\rangle \\ & - 2\langle sx|xs\rangle + 2\langle xx|xx\rangle + 4\langle xy|xy\rangle - 2\langle xy|yx\rangle \\ & + 2\langle xx|yy\rangle + 2\langle sxx|sxx\rangle + 4\langle sxy|sxy\rangle \\ & - 2\langle sxy|syx\rangle + 2\langle sxx|syy\rangle + 4\langle xyy|xyy\rangle \\ & + 4\langle xyy|xzz\rangle \qquad (II.11)\end{aligned}$$

$$\begin{aligned}E[{}^2\mathrm{D(sp^4)}] = {}& E_c + \langle s|s\rangle + 4\langle x|x\rangle + 4\langle sx|sx\rangle \\ & - 2\langle sx|xs\rangle + \langle xx|xx\rangle + 5\langle xy|xy\rangle - \langle xy|yx\rangle \\ & + \langle sxx|sxx\rangle + 5\langle sxy|sxy\rangle - \langle sxy|syx\rangle \\ & + 2\langle xyy|xyy\rangle + 2\langle xyz|xyz\rangle + 2\langle xyz|xzy\rangle \qquad (II.12)\end{aligned}$$

$$\begin{aligned}E[{}^4\mathrm{P(sp^4)}] = {}& E_c + \langle s|s\rangle + 4\langle x|x\rangle + 4\langle sx|sx\rangle \\ & - 3\langle sx|xs\rangle + \langle xx|xx\rangle + 5\langle xy|xy\rangle - 3\langle xy|yx\rangle \\ & + \langle sxx|sxx\rangle + 5\langle sxy|sxy\rangle - 3\langle sxy|syx\rangle \\ & - 3\langle sxy|xsy\rangle + 2\langle xyy|xyy\rangle + 2\langle xyz|xyz\rangle \\ & - 2\langle xyz|xzy\rangle \qquad (II.13)\end{aligned}$$

$$\begin{aligned}E[{}^2\mathrm{D^o(s^2p^3)}] = {}& E_c + 2\langle s|s\rangle + 3\langle x|x\rangle + \langle ss|ss\rangle \\ & + 6\langle sx|sx\rangle - 3\langle sx|xs\rangle + 3\langle xy|xy\rangle + 3\langle ssx|ssx\rangle \\ & + 6\langle sxy|sxy\rangle - \langle xyy|xzz\rangle + \langle xyy|xyy\rangle \qquad (II.14)\end{aligned}$$

$$\begin{aligned}E[{}^4\mathrm{S^o(s^2p^3)}] = {}& E_c + 2\langle s|s\rangle + 3\langle x|x\rangle + \langle ss|ss\rangle \\ & + 6\langle sx|sx\rangle - 3\langle sx|xs\rangle + 3\langle xy|xy\rangle - 3\langle xy|yx\rangle \\ & + 3\langle ssx|ssx\rangle + 6\langle sxy|sxy\rangle - 6\langle sxy|syx\rangle \\ & + \langle xyz|xyz\rangle - 2\langle xyz|xzy\rangle \qquad (II.15)\end{aligned}$$

$$\left.\begin{matrix}E[{}^2\mathrm{P^o(p^5)}] \\ E[{}^2\mathrm{P^o(s^2p^3)}]\end{matrix}\right]\begin{matrix}+\\-\end{matrix} =$$

$$\begin{aligned}& E_c + \langle s|s\rangle + 4\langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 3\langle sx|sx\rangle \\ & - \tfrac{3}{2}\langle sx|xs\rangle + \tfrac{3}{2}\langle xx|xx\rangle + 5\langle xy|xy\rangle - \tfrac{5}{2}\langle xy|yx\rangle \\ & + \tfrac{1}{2}\langle xx|yy\rangle + \tfrac{3}{2}\langle ssx|ssx\rangle + 2\langle sxy|sxy\rangle \\ & - \langle sxy|syx\rangle + \langle sxx|sxx\rangle + \langle sxx|syy\rangle + \tfrac{7}{2}\langle xyy|xyy\rangle \\ & + \tfrac{1}{2}\langle xyy|xzz\rangle + 2\langle xyz|xyz\rangle - \langle xyz|xzy\rangle \pm [(\langle s|s\rangle \\ & - \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 3\langle sx|sx\rangle - \tfrac{3}{2}\langle sx|xs\rangle \\ & - \tfrac{1}{2}\langle xx|xx\rangle - 3\langle xy|xy\rangle + \tfrac{3}{2}\langle xy|yx\rangle + \tfrac{1}{2}\langle xx|yy\rangle \\ & + \tfrac{3}{2}\langle ssx|ssx\rangle + 2\langle sxy|sxy\rangle - \langle sxy|syx\rangle + \langle sxx|sxx\rangle \\ & + \langle sxx|syy\rangle - \tfrac{5}{2}\langle xyy|xyy\rangle + \tfrac{1}{2}\langle xyy|xzz\rangle \\ & - 2\langle xyz|xyz\rangle + \langle xyz|xzy\rangle)^2 + 2(\langle ss|xx\rangle \\ & + 3\langle xyy|xss\rangle)^2]^{1/2} \qquad (II.16)\end{aligned}$$

$$N_v = 6$$

$$\begin{aligned}E[{}^1\mathrm{P^o(sp^5)}] = {}& E_c + \langle s|s\rangle + 5\langle x|x\rangle + 5\langle sx|sx\rangle \\ & - \langle sx|xs\rangle + 8\langle xy|xy\rangle - 4\langle xy|yx\rangle + 2\langle xx|xx\rangle \\ & + 2\langle sxx|sxx\rangle + 8\langle sxy|sxy\rangle - 4\langle sxy|syx\rangle \\ & + 6\langle sxy|xsy\rangle + 6\langle xyy|xyy\rangle + 4\langle xyz|xyz\rangle \\ & - 2\langle xyz\langle xzy\rangle \qquad (II.17)\end{aligned}$$

$$\begin{aligned}E[{}^3\mathrm{P^o(sp^5)}] = {} & E_\mathrm{c} + \langle s|s\rangle + 5\langle x|x\rangle + 5\langle sx|sx\rangle \\ & - 3\langle sx|xs\rangle + 8\langle xy|xy\rangle - 4\langle xy|yx\rangle + 2\langle xx|xx\rangle \\ & + 2\langle sxx|sxx\rangle + 8\langle sxy|sxy\rangle - 4\langle sxy|syx\rangle \\ & - 2\langle sxy|xsy\rangle + 6\langle xyy|xyy\rangle + 4\langle xyz|xyz\rangle \\ & - 2\langle xyz|xzy\rangle \end{aligned} \tag{11.18}$$

$$\begin{aligned}E[{}^1\mathrm{D(s^2p^4)}] = {} & E_\mathrm{c} + 2\langle s|s\rangle + 4\langle x|x\rangle + \langle ss|ss\rangle \\ & + 8\langle sx|sx\rangle - 4\langle sx|xs\rangle + \langle xx|xx\rangle + 5\langle xy|xy\rangle \\ & - \langle xy|yx\rangle + 4\langle ssx|ssx\rangle + 2\langle sxx|sxx\rangle \\ & + 10\langle sxy|sxy\rangle - 2\langle sxy|syx\rangle + 2\langle xyy|xyy\rangle \\ & + 2\langle xyz|xyz\rangle + 2\langle xyz|xzy\rangle \end{aligned} \tag{11.19}$$

$$\begin{aligned}E[{}^3\mathrm{P(s^2P^4)}] = {} & E_\mathrm{c} + 2\langle s|s\rangle + 4\langle x|x\rangle + \langle ss|ss\rangle \\ & + 8\langle sx|sx\rangle - 4\langle sx|xs\rangle + \langle xx|xx\rangle + 5\langle xy|xy\rangle \\ & - 3\langle xy|yx\rangle + 4\langle ssx|ssx\rangle + 2\langle sxx|sxx\rangle \\ & + 10\langle sxy|sxy\rangle - 6\langle sxy|syx\rangle + 2\langle xyy|xyy\rangle \\ & + 2\langle xyz|xyz\rangle - 2\langle xyz|xzy\rangle \end{aligned} \tag{11.20}$$

$$\begin{aligned}\left.\begin{matrix}E[{}^1\mathrm{S(p^6)}] \\ E[{}^1\mathrm{S(s^2p^4)}]\end{matrix}\right]\begin{matrix}+\\-\end{matrix} = {} & \\ & E_\mathrm{c} + \langle s|s\rangle + 5\langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 4\langle sx|sx\rangle \\ & - 2\langle sx|xs\rangle + \tfrac{5}{2}\langle xx|xx\rangle + 8\langle xy|xy\rangle - 4\langle xy|yx\rangle \\ & + \langle xx|yy\rangle + 2\langle ssx|ssx\rangle + 2\langle sxx|sxx\rangle + 4\langle sxy|sxy\rangle \\ & - 2\langle sxy|syx\rangle + 2\langle sxx|syy\rangle + 8\langle xyy|xyy\rangle \\ & + 2\langle xyy|xzz\rangle + 4\langle xyz|xyz\rangle - 2\langle xyz|xzy\rangle \pm [(\langle s|s\rangle \\ & - \langle x|x\rangle + \tfrac{1}{2}\langle ss|ss\rangle + 4\langle sx|sx\rangle - 2\langle sx|xs\rangle \\ & - \tfrac{1}{2}\langle xx|xx\rangle - 4\langle xy|xy\rangle + 2\langle xy|yx\rangle + \langle xx|yy\rangle \\ & + 2\langle ssx|ssx\rangle + 2\langle sxx|sxx\rangle + 4\langle sxy|sxy\rangle \\ & - 2\langle sxy|syx\rangle + 2\langle sxx|syy\rangle - 4\langle xyy|xyy\rangle \\ & + 2\langle xyy|xzz\rangle - 4\langle xyz|xyz\rangle + 2\langle xyz|xzy\rangle)^2 \\ & + 3(\langle ss|xx\rangle + 4\langle xyy|xss\rangle)^2]^{1/2} \end{aligned} \tag{11.21}$$

$$N_\mathrm{v} = 7$$

$$\begin{aligned}E[{}^2\mathrm{S(sp^6)}] = {} & E_\mathrm{c} + \langle s|s\rangle + 6\langle x|x\rangle + 6\langle sx|sx\rangle \\ & - 3\langle sx|xs\rangle + 3\langle xx|xx\rangle + 12\langle xy|xy\rangle - 6\langle xy|yx\rangle \\ & + 3\langle sxx|sxx\rangle + 12\langle sxy|sxy\rangle - 6\langle sxy|syx\rangle \\ & + 12\langle xyy|xyy\rangle + 8\langle xyz|xyz\rangle - 4\langle xyz|xzy\rangle \end{aligned} \tag{11.22}$$

$$\begin{aligned}E[{}^2\mathrm{P^o(s^2p^5)}] = {} & E_\mathrm{c} + 2\langle s|s\rangle + 5\langle x|x\rangle + \langle ss|ss\rangle \\ & + 10\langle sx|sx\rangle - 5\langle sx|xs\rangle + 2\langle xx|xx\rangle + 8\langle xy|xy\rangle \\ & - 4\langle xy|yx\rangle + 5\langle ssx|ssx\rangle + 4\langle sxx|sxx\rangle \\ & + 16\langle sxy|sxy\rangle - 8\langle sxy|syx\rangle + 6\langle xyy|xyy\rangle \\ & + 4\langle xyz|xyz\rangle - 2\langle xyz|xzy\rangle \end{aligned} \tag{11.23}$$

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