Use of second-moment constraints for the refinement of determinantal wave functions

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A constrained least-squares fit procedure wherein the integral $\int [\rho(\mathbf{r}) - \rho_0(\mathbf{r})]^2 d\mathbf{r}$ is minimized [$\rho_0(\mathbf{r})$ is the reference near–Hartree-Fock (NHF) electron density distribution and $\rho(\mathbf{r})$ is the refined one obtained from a single Slater determinant] has been developed. The constraints applied are the exact theoretical $\langle p^2 \rangle$ and $\langle r^2 \rangle$ expectation values. These expectation values are expected to tailor the electron density around the nuclear and tail regions, respectively. The procedure has been applied to lithium and beryllium atoms as test cases. Nearly all the $\langle r^n \rangle$ and $\langle p^n \rangle$ (for $n = -2, -1, 1, 3, 4,$ and 5) expectation values have been improved with use of this procedure. The sacrifice in the electronic energy, in comparison to the corresponding NHF one, is about 0.02% in both cases.

I. INTRODUCTION

The Hartree-Fock (HF) method has been applied successfully to a variety of quantum-chemical problems during the last 40 years or so. The application of this method, which provides a standard benchmark in quantum-chemical literature, to fairly large systems of atoms and molecules has become feasible due to the advent of powerful computers. However, computationally or conceptually more complicated methods such as configuration-interaction (CI), multiconfiguration self-consistent-field (MCSCF), many-body perturbation theory (MBPT), or the coupled-cluster method, have to be resorted to for obtaining highly accurate wave functions. The density functional method which employs the electron density as a basic variable has, of late, become quite popular for solutions of atomic-, molecular-, and solid-state problems. However, here one loses the simplicity associated with a single Slater-determinantal wave function also. In this light, Massa and others[1–4] have recently developed a novel method to estimate the "wave function" of a system. Using experimental data of x-ray diffraction pattern, the wave functions of beryllium atom, beryllium metal, and the H_2 molecule in the form of a Slater determinant has been obtained by them.[1–4]. The corresponding electron density naturally satisfies the condition of N representability, i.e., there exists at least one antisymmetric N-electron wave function giving rise to the given electron density. The computation of other expectation values is readily possible within this method. Let $F_{obs}(\mathbf{k})$ be the experimental x-ray structure factor, and $F_{cal}(\mathbf{k})$ the calculated one [$F(\mathbf{k})$ is the fourier transform of electron density]. In the method proposed in Refs. 1–4, the sum $\sum_k [F_{obs}(\mathbf{k}) - F_{cal}(\mathbf{k})]^2$ is minimized by the least-squares method (note that the least-squares method was first used by Stewart[5] to obtain a Gaussian basis set for hydrogen atom). The above difference is minimized by varying the matrix elements P_{ij} of the calculated distribution $F_{cal}(\mathbf{k})$, i.e.,

$$F_{cal}(\mathbf{k}) = \sum_{i,j} P_{ij} \int \Psi_i(\mathbf{r}) \Psi_j(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \ . \tag{1}$$

Here, P_{ij} are the elements of the charge density-bond order matrix and they are varied subject to the constraint that they form a matrix which is normalized, Hermitian, and idempotent.

The advantage of the above procedure is that the wave function is still a single Slater-determinant, which is a cornerstone of the HF approximation. Although the HF wave function, by definition, gives the best value for the total energy offered by single-determinantal functions, "too much emphasis has been placed on total energy for assessing the quality of a wave function in the literature."[4] Massa and Frishberg[1,3] and Massa[4] have shown that the x-ray fitted wave function gives better results than the HF wave function for most of the expectation values, with only a little sacrifice in the total energy. The drawback of this method is that it requires entire experimental data for $F(\mathbf{k})$ as the input. This need is obviated in the method proposed in the present work (see Sec. II).

Yet another simple model has been developed recently by Gadre and Gejji[6,7] for refinement of a *three-dimensional* probability distribution. If $F(\mathbf{x})$ is a given distribution, a refined distribution $H(\mathbf{x})$ is to be found which is "close" to the original distribution. Let

$$H(\mathbf{x}) = F(\mathbf{x})G(\mathbf{x}) \ , \tag{2}$$

where $G(\mathbf{x})$ is a multiplicative function determined by minimizing the integral $\int [G(\mathbf{x}) - 1]^2 d\mathbf{x}$, subject to the constraints

$$\int H(\mathbf{x}) d\mathbf{x} = N \tag{3}$$

and

$$\int H(\mathbf{x}) x^2 d\mathbf{x} = \langle x^2 \rangle \ , \tag{4}$$

where N is the number of electrons and $\langle x^2 \rangle$ is the second moment. A standard variational treatment leads to the solution

$$G(\mathbf{x}) = 1 + F(\mathbf{x})(\lambda + \mu x^2) \ , \tag{5}$$

where λ and μ are the respective Lagrange multipliers. The results obtained by them[7] for beryllium through

neon atoms were found to be fairly accurate, compared to either experimental or best theoretical ones. The advantage of the above procedure is that it is a relatively simple procedure involving linear equations alone for refining any given probability distribution. The drawback is that the refined distribution could become negative in some region[8] and the weightages which can be used are not necessarily unique.

In the present work, the authors have used a combination of the above two procedures to refine a given determinental wave function. The integral $\int [\rho(\mathbf{r}) - \rho_0(\mathbf{r})]^2 d\mathbf{r}$ is minimized [$\rho(\mathbf{r})$ and $\rho_0(\mathbf{r})$ are, respectively, the refined and starting density distributions] subject to the second-moment constraints. The procedure is discussed in detail in Sec. II.

II. PROCEDURE

In this work the starting wave function is refined using a constrained least-squares procedure. The starting wave functions used were those of Huzinaga,[9] viz., 10G (ten-Gaussian) basis-set for beryllium and 9G basis-set for lithium. The integral

$$K = \int [\rho(\mathbf{r}) - \rho_0(\mathbf{r})]^2 d\mathbf{r} \qquad (6)$$

is minimized where ρ_0 is the starting electron density and ρ is the refined one.

The constraints employed are those of experimental $\langle r^2 \rangle$ and $\langle p^2 \rangle$ expectation values since the former expectation value is expected to refine the tail of the Gaussian in position space and the latter is expected to improve the Gaussian near the nucleus. The parameters were optimized subject to orthonormality, ensuring that the resulting wave function is still a single Slater determinant. Thus this work represents a combination of the above outlined procedures.[1,3,6,7] The parameters, viz., the linear coefficients as well as exponents, were varied within $\pm 10\%$ of their original values.[9] The optimization was carried out by employing subroutine STEPIT,[10] which is a general optimization routine which finds local minima of a real function of several variables.

For Be, Bunge's[11] CI-theoretical $\langle r^2 \rangle$ and $\langle p^2 \rangle$ constraints were used, and for Li, Banyard's[12] $\langle p^2 \rangle$ (experimental) and Gupta and Boyd's[13] (theoretical) values were used as constraints. From the optimized set of parameters, $\langle r^n \rangle$ and $\langle p^n \rangle$ (where $n = -2, -1, 1, 2, 3, 4, 5$) expectation values were calculated. Then $\rho(r)$ (density in position space) and $\gamma(p)$ (density in momentum space) were computed using the same set of parameters. The results and comparison with literature values are presented in Sec. III.

III. RESULTS AND DISCUSSION

Table I compares the $\langle r^n \rangle$ and $\langle p^n \rangle$ expectation values computed with the refined distribution and those computed with the original Huzinaga[9] 9G basis set for lithium. In Table II a similar comparison of expectation values of the beryllium atom using the refined distribution and Huzinaga's[9] 10G basis set is presented. Table II

TABLE I. Expectation values for the Li atom 9G basis sets (all values in a.u.).

Expectation values	Huzinaga[a] 9G	Refined[b] 9G	Correlated[c]
$\langle r^{-2} \rangle$	30.146	30.244	30.246
$\langle r^{-1} \rangle$	5.715	5.733	5.718
$\rho(0)$	13.039	13.154	13.867
$\langle r \rangle$	5.018	4.994	4.994
$\langle r^2 \rangle$	18.601	18.372	18.372
$\langle r^3 \rangle$	94.27	92.16	92.44
$\langle r^4 \rangle$	559.9	540.6	545.8
$\langle r^5 \rangle$	11 171.1	10 752.2	
$\langle p^{-2} \rangle$	26.12	25.65	
$\langle p^{-1} \rangle$	5.166	5.128	5.149
$\gamma(0)$	8.103	7.973	
$\langle p \rangle$	4.905	4.925	
$\langle p^2 \rangle$	14.862	14.956	14.956
$\langle p^3 \rangle$	70.84	71.16	
$\langle p^4 \rangle$	592.4	587.2	
$\langle 1/r_{ij} \rangle$	2.281	2.525	2.199
Energy	-7.4323	-7.4317	-7.4780

[a]Values computed from Huzinaga's 9G (nine-Gaussian) basis set (Ref. 9).
[b]Values computed in present work.
[c]See Ref. 12.

also displays the expectation values computed by Frishberg[4] and Bunge.[11]

From Table I it is clear that most of the properties obtained in the present work have improved; for example, $\langle r^{-2} \rangle$ and $\langle r \rangle$ expectation values of present basis are nearly the same as the correlated one, typical deviations from the latter ones being less than 0.01%.

Further, it will be noted that the $\langle r^3 \rangle$ and $\langle r^4 \rangle$ expectation values have improved dramatically. All the properties for the Li atom in coordinate space examined in the present study, except for $\langle r^{-1} \rangle$, have improved. The wave function obtained using Huzinaga's basis is comparable to the NHF wave function, but the wave function obtained by constraining $\langle r^2 \rangle$ and $\langle p^2 \rangle$ expectation values to the exact values is closer to the exact wave function, and the loss in energy is less than 0.01%, with respect to the Huzinaga 9G basis, which is insignificant.

In the case of the beryllium atom, as is shown in Table II, if one goes through all $\langle r^n \rangle$ properties, the same trends as in lithium are seen. The improvement is especially remarkable in $\langle r^3 \rangle$, $\langle r^4 \rangle$, and $\langle r^5 \rangle$ which clearly indicates that the refined wave function mimics the exact one more closely than any other NHF quality wave functions in the literature. Here also the loss in energy is a mere 0.02%. On comparison with all $\langle r^n \rangle$ expectation values, the present electron density distribution is found to be comparable to the value of Frishberg[4] in the tail region, as reflected by the $\langle r^3 \rangle$, $\langle r^4 \rangle$, and $\langle r^5 \rangle$ expectation values.

The $\langle p^n \rangle$ expectation values for Be in Table II are self-explanatory of the success of the above method. The $\langle p \rangle$ expectation value is closer to the correlated one and $\langle p^3 \rangle$ is nearly identical to the respective correlated mo-

TABLE II. Expectation values for the Be atom 10G basis set (all values in a.u.).

Expectation values	Huzinaga[a] 10G	Frishberg[b]	Refined[c] 10G	Correlated[d]
$\langle r^{-2} \rangle$	57.56	57.63	57.49	57.59
$\langle r^{-1} \rangle$	8.408	8.425	8.450	8.425
$\rho(0)$	34.082		33.612	
$\langle r \rangle$	6.126	5.988	5.963	5.978
$\langle r^2 \rangle$	17.28	16.32	16.28	16.28
$\langle r^3 \rangle$	62.76		57.25	56.95
$\langle r^4 \rangle$	266.6	231.6	235.7	233.1
$\langle r^5 \rangle$	1283.7	1065.5	1102.0	1085.96
$\langle p^{-2} \rangle$	24.86		23.40	
$\langle p^{-1} \rangle$	6.291		6.114	
$\gamma(0)$	5.7067		5.217	
$\langle p \rangle$	7.435		7.507	7.529[e]
$\langle p^2 \rangle$	29.144	29.19	29.33	29.33
$\langle p^3 \rangle$	185.4		184.8	186.24[e]
$\langle p^4 \rangle$	2091.5	2165.5	2050.3	2029.1[e]
$\langle 1/r_{ij} \rangle$	4.489	4.538	4.566	4.380
Energy	-14.572	-14.572	-14.569	-14.667

[a]Values computed from Huzinaga's 10G basis set (Ref. 9).

[b]See Ref. 4.

[c]Values computed in the present work.

[d]See Ref. 11.

[e]Values computed by integrating appropriately weighted difference of correlated and NHF Compton profiles (Ref. 14). The value of this integral was added to the value of $\langle p^n \rangle_{NHF}$. However, $\langle p^4 \rangle$ estimated this way is rather unreliable due to the inadequacy of the available $J(q)$ data in the high-q region.

ment. The $\langle p^{-1} \rangle$ expectation value is also in the correct direction in comparison with the correlated value.

An interesting observation in the case of the lithium atom is that the values of $\rho(0)$, the density at $r = 0$ in coordinate space, has also improved. Hence it can be concluded that the entire distribution has been generally improved with a negligible loss in energy.

Thus, here is a novel method of generating a property-oriented wave function, using just two experimentally measurable quantities, viz., the second moments $\langle r^2 \rangle$ and $\langle p^2 \rangle$. It yields almost all properties better than the currently available NHF ones in the literature, at a loss of less than 0.02% in the energy. The present method ensures that the electron densities in both the spaces are always non-negative and thus remedies a drawback of the earlier refinement procedure.[8] The present procedure is expected to be particularly useful for the generation of molecular Gaussian basis sets. The results in the present study point towards a wider scope and better applicability of this method.

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