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Determination of Molecular Properties by the Method of Moments

IV. Scattering Problems

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The method of moments and the method of least squares is applied to electron scattering on a simple model potential. Some general problems connected with treatment of scattering problems by the method of moments and the method of least squares are discussed. The calculations give an example of the "random sampling type" error estimates discussed in previous papers of the series, and present a possible way of optimizing nonlinear parameters in the framework of the method of moments and the method of least squares.

Die Momentenmethode und die Methode der kleinsten Quadrate wird auf die Elektronenstreuung an einem einfachen Modellpotential angewandt. Einige allgemeine Probleme bei der Anwendung dieser beiden Methoden auf Streuprobleme wurden diskutiert. Die Berechnungen geben ein Beispiel der Fehlerabschätzung vom „Stichproben-Typ", der in vorhergehenden Artikeln dieser Serie untersucht wurde; sie stellen eine Möglichkeit der Optimierung nicht-linearer Parameter bei den genannten zwei Methoden dar.

La méthode des moments et la méthode des moindres carrés sont appliquées à l'étude de la diffusion électronique sur un potentiel modèle simple. Discussion de certains problèmes généraux liés à l'emploi de ces méthodes à l'étude de la diffusion. Les calculs donnet un exemple de l'estimation d'erreur par échantillonage discutée dans les articles précédents, et présentent une méthode pour optimiser des paramètres non linéaires dans le cadre des méthodes des moments et des moindres carrés.

1. Introduction

Scattering and bound-state problems have many common features and moment-type methods appear to be well suited for solving them. Nevertheless the differences between the two types of problems make it necessary to discuss the treatment of scattering problems in some detail[1].

Let $\boldsymbol{H}$ be the Hamiltonian operator of a molecular system and $\psi(x)$ an eigenfunction of $\boldsymbol{H}$ belonging to the eigenvalue E, x denoting a point of the configurational space

$$(\boldsymbol{H} - E)\,\psi(x) = 0\,. \tag{1}$$

If $\psi(x)$ describes a scattering state, its asymptotic behaviour is plane-wave like in certain directions of the configurational space.

Let $\varphi(x, \alpha)$ be a variational wave function depending on the variational parameters $\alpha = \{\alpha_1, \alpha_2, \ldots, \alpha_n\}$ and let $w_0(x)$, $w_1(x), \ldots, w_n(x), \ldots$ be a set of linearly independent functions to be referred to as weight functions.

[1] The previous papers of this series [1] will be referred to as I, II and III.

Let us consider the moments

$$m_i(\alpha, \mathscr{E}) = \langle w_i(x) | \boldsymbol{H} - \mathscr{E} | \varphi(x, \alpha) \rangle \tag{2}$$

of $(\boldsymbol{H} - \mathscr{E})\,\varphi(x, \alpha)$, $\mathscr{E}$ denoting approximation to E.

The method of moments determines the values of the variational parameters and $\mathscr{E}$ from the requirements

$$\langle w_i | \boldsymbol{H} - \mathscr{E} | \varphi \rangle = 0 \tag{3}$$

with $i = 0, 1, \ldots, n$, or, if the value of $\mathscr{E}$ is prescribed (this may be often the case in scattering problems) then with $i = 1, 2, \ldots, n$. Although one has considerable freedom in the choice of the weight functions, in the case of bound-state problems the set

$$w_0 \approx \varphi; \qquad w_i \approx \partial\varphi/\partial\alpha_i \tag{4}$$

appears to be one of the best ones and in the previous papers of the series in practice always this approach has been considered. The remaining freedom in the choice of the weight functions can efficiently be used to reduce difficulties of integration.

In scattering problems, however, it appears advantageous to consider slightly different possibilities.

As φ has a plane-wave like asymptotic behaviour in certain directions, in the case of weight functions of the form (4) the integrals (2) involve divergent terms. Even if the sum of these divergent terms is finite, for interacting many-particle systems (in particular without geometrical symmetry), the calculation of the integrals may require inconvenient cut-off and/or limiting processes. Consequently it appears advantageous to require that the weight functions should be quadratically integrable. In the following quadratically integrable weight functions will be considered.

In the case of quadratically integrable weight functions there exits some danger that the weight functions will insufficiently scan the regions far from the scattering center. The application of the method of moments may also result in spurious singularities in the phase shifts similar to those discussed by Nesbet [2] in connection with the Harris approach [3]. Although there are possibilities in the framework of the method of moments to avoid these difficulties (consider the stability tests to be discussed below) but it may be advantageous to avoid them by choosing more weight functions than variational parameters in φ. This means that the variational parameters may be determined by the method of least squares from the equation

$$\lambda = \sum_{i=0}^{K>n} |c_i \langle w_i(x) | \boldsymbol{H} - \mathscr{E} | \varphi(x, \alpha) \rangle|^2 = \min, \tag{5}$$

where the weight functions w_i and the trial function φ are to be subjected to convenient normalization conditions (the c_i's denote non-zero weight factors[2,3]). For potential scattering the normalization conditions will be fixed in Section 3.

[2] Although the c_i's may be included in the normalization factors of the weight functions it can have advantages to write them out explicity. E.g. one possible way of carrying out the stability tests to be discussed below is to vary the c_i's.

[3] It has been shown in I that Eq. (5) is essentially a mathematically convenient approximation to the equation proposed by Preuss [4].

Obviously the well-known possibilities provided by the method of moments for the reduction of difficulties of integration are not lost by using the method of least squares.

Alternative moment-type approaches to scattering problems have also been considered by Harris [3]. A similar approach has been applied by Ladányi to the Bethe-Salpeter equations [3]. A detailed analysis of scattering methods has recently been given by Nesbet [2].

2. The Accuracy of the Results

Evidently one single calculation can hardly give any information about the accuracy of the obtained wave function φ. In order to obtain an estimate of the error in φ or rather of the error in some physical quantity calculated from φ (say, the error in a matrix element of the form $\langle\varphi|\boldsymbol{L}|\varphi\rangle$) a systematical series of calculations must be carried out. In such a series, if possible, both the weight functions and the kind and number of parameters in φ must be changed. In addition, these changes must be such that they can considerably influence φ in those regions of the configurational space which are important for the value of the physical property under consideration[4]. In this case it has a low probability that in every approximation the error in the physical property will be approximately the same both in magnitude and in sign. Thus the oscillations of the physical property will give an estimate of its error in the sense of mathematical statistics. The reliability of this estimate rapidly increases with the increase of the number of different calculations[5].

Such stability tests are certainly more tiresome than the calculation of one single approximate wave function. Nevertheless if complicated systems are investigated which can not be easily subjected to accurate measurement (scattering state is a good example) and thus semiempirical error estimates are impossible it appears improbable that any other error estimate will be simpler than such stability tests. In any case the stability tests give a deep insight into the reliability of the approximation.

In practical calculations it may obviously turn out that somewhat simpler tests of the accuracy of φ will work. E. g. it can be expected that the average of the overlap integrals between different approximations to ψ may give a good estimate of the "overall" stability and thus the "overall" accuracy of φ. In any case, such error estimates must always be handled with care.

The above considerations have an interesting consequence. Although both the method of moments and the method of least squares are able to determine nonlinear parameters, their application is evidently considerably simpler if only linear parameters are optimized. The task of optimizing nonlinear parameters can, however, often be reduced to the task of optimizing linear ones if we regard as the "best" values of the nonlinear parameters those which ensure the maximum stability of the wave function against the introduction of further linear parameters.

[4] Qualitatively speaking the changes must be able to influence φ in those regions where $|\boldsymbol{L}\psi|$ is large.

[5] It may be instructive to compare these considerations with the idea of "guided approximations" (Preuss, Schwartz, Hirschfelder, Epstein, Coulson, Hall, Szondy and others). References are given in I.

In this case the optimization of the nonlinear parameters can be combined with the stability test[6].

Within the framework of the method of least squares the condition

$$\partial\lambda(\alpha)/\partial\alpha_i = 0 \tag{6}$$

(α_i nonlinear parameter) may lead to a reasonable choice of the nonlinear parameters if the use of the corresponding basis set results in a satisfactory stability of the approximate solutions.

If many nonlinear parameters are to be optimized, this must in general be done also in this case by relaxation methods or other methods for seeking extrema.

3. The Results of the Test Calculations

Potential scattering on a simple model potential (Nesbet [2]) has been investigated. The Schrödinger equation to be solved for the scattered wave with angular momentum l has the form

$$-\frac{1}{2}\frac{1}{r}\frac{\mathrm{d}^2(r\psi_l(r))}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2}\psi_l(r) - e^{-r}\psi_l(r) = E\psi_l(r)\,. \tag{7}$$

The variational wave function has been taken in the form

$$\varphi(x,\alpha) = \sum_{i=1}^{n} \alpha_i \varphi_i(x)\,, \tag{8}$$

where

$$\varphi_1(x) = \sin(kr)/(kr)\,(1-\exp(-\gamma_2 r))^l\,, \tag{9}$$

$$\varphi_2(x) = \cos(kr)/(kr)\,(1-\exp(-\gamma_2 r))^{l+1}\,, \tag{10}$$

$$\varphi_i(x) = r^{l+i-3}\exp(-\gamma_1 r) \quad \text{for} \quad i \geqq 3\,, \tag{11}$$

and

$$k = \sqrt{2E}\,. \tag{12}$$

The weight functions have been chosen as

$$w_i(r) = \sqrt{\beta^{2i+1}/(2i)!}\; r^{i-1}\exp(-\beta r) \qquad (i = 1, 2, \ldots, K)\,. \tag{13}$$

The wave function (8) behaves correctly both at $r=0$ and $r=\infty$. For $l=0$ it can, for good values of γ_1 and γ_2, be expected to be a very good trial function. However, for $l>0$ it is less suitable for approximating to the exact solution of (7) as this would require Bessel-type functions instead of the harmonical ones[7]. Thus our trial function provides an example for all the interesting cases: a very good trial function gradually changing into a bad trial function as l increases. The numerical results clearly indicate this change.

The wave function has been normalized according to

$$\alpha_1^2 + \alpha_2^2 = 1\,, \tag{14}$$

[6] It should be noted that it is not always possible to decide uniquely from data obtained by stability test which value of a nonlinear parameter is the "best" one. This means, however, that simply the answer is not unique and we can choose practically any value within some interval. The results presented in Table 2 give a good example of this effect.

[7] Naturally for very high values of n our trial function tends to the exact solution.

i.e. the electron fluxus at $r=\infty$ has been fixed. Requirement (5) subject to the "normalization condition" (14) yields the secular equation

$$\begin{vmatrix} A_{11}-\lambda & A_{12} & A_{13} & \dots & A_{1n} \\ A_{21} & A_{22}-\lambda & A_{23} & \dots & A_{2n} \\ A_{31} & A_{32} & A_{33} & \dots & A_{3n} \\ \dots & \dots & \dots & \dots & \dots \\ A_{n1} & A_{n2} & A_{n3} & \dots & A_{nn} \end{vmatrix} = 0 \tag{15}$$

with

$$A_{ij} = \sum_{h=1}^{K} \langle \varphi_i(x) | \boldsymbol{H} - E | w_h(x) \rangle \, c_h^* c_h \langle w_h(x) | \boldsymbol{H} - E | \varphi_j(x) \rangle \,. \tag{16}$$

The secular equation (15) and the corresponding set of homogeneous linear equations determining the α_i's have been solved by a Gauss-Jordan type elimination in which the first two columns and rows were not allowed to appear as pivotal columns and rows, respectively.

The results given in Table 1 have all been obtained with trial functions with $\gamma_1 = \gamma_2 = \gamma$ and weight functions with $\beta = 1.0$, and $c_i = 1.0$. 5 different approximations have been calculated for every value of l, k and γ in which φ involved 4, 6, 8, 10 and 12 terms ($n = 4, 6, 8, 10$ and 12). These approximations will be referred to as the 1 st, ..., 5 th. In calculations with the method of moments (MM) the number of weight functions w_h has to be fixed by $K = n - 1$; the least-squares (LS) approximations included in Table 1 have been computed by choosing $K = n + 2$.

A high number of calculations not included in Table 1 has been carried out covering wide ranges of different parameters without considerably changing the overall picture.

The values λ_i included in Table 1 are defined in Eq. (5), the subscript referring to the i th approximation. The values S_{ij} included in Table 1 are defined by

$$S_{ij} = \frac{\left| \int_0^R \mathrm{d}r r^2 \varphi^{(i)*}(r) \, \varphi^{(j)}(r) \right|^2}{\int_0^R \mathrm{d}r r^2 |\varphi^{(i)}(r)|^2 * \int_0^R \mathrm{d}r r^2 |\varphi^{(j)}(r)|^2} \tag{17}$$

the superscripts i and j again refer to the corresponding approximation. Thus the values S_{ij} present an example for an "overall" (and rather sensitive[8,9]) stability test. The upper limit R of the integrals has been chosen in such a way that it should include regions both in the neighbourhood and far from the scattering center. (The results included in Table 1 have been calculated with $R = 39.6$).

The quantities S_{3e} and S_{5e} included in Table 1 give the overlap between the wave functions of the 3rd and 5th approximation and the exact wave functions obtained by a numerical integration of (7).

[8] The phase shifts appear in general less characteristic of the "overall" accuracy of the wave functions, as they depend only on the values α_1 and α_2.

[9] For higher values of k the approximations are slightly better than for the k-values given in Table 1.

Table 1. *Values of the quantities* λ_i *and* $S_{i,i+1}$

	γ	λ_1	S_{12}	λ_2	S_{23}	λ_3	S_{34}	λ_4	S_{45}	λ_5	S_{3e}	S_{5e}
MM	4.00	0	0.9976	0	0.9998	0	0.9988	0	0.9534	0	0.9999	0.9449
	2.00	0	0.9999	0	0.9999	0	1.0000	0	1.0000	0	1.0000	1.0000
$l=0$	1.00	0	0.9995	0	0.9999	0	0.9999	0	1.0000	0	0.9999	1.0000
	0.50	0	0.8284	0	0.6900	0	0.9161	0	0.3455	0	0.9290	0.3430
$k=0.2$	0.25	0	0.0791	0	0.4884	0	0.8340	0	0.9240	0	0.1773	0.0013
LS	4.00	$2_{10}-2$	0.9986	$3_{10}-5$	0.9996	$2_{10}-7$	0.9920	$1_{10}-8$	0.9158	$1_{10}-10$	0.9999	0.8916
	2.00	$3_{10}-5$	0.9999	$5_{10}-7$	0.9999	$1_{10}-9$	1.0000	$7_{10}-13$	1.0000	$1_{10}-16$	1.0000	1.0000
$l=0$	1.00	$2_{10}-4$	0.9998	$9_{10}-10$	0.9999	$2_{10}-10$	1.0000	$6_{10}-13$	1.0000	$1_{10}-15$	1.0000	1.0000
	0.50	$5_{10}-3$	0.9808	$2_{10}-5$	0.9487	$4_{10}-8$	0.9897	$2_{10}-12$	0.9838	$1_{10}-12$	0.9841	0.9943
$k=0.2$	0.25	$8_{10}-3$	0.2005	$5_{10}-6$	0.5417	$5_{10}-9$	0.8371	$2_{10}-12$	0.8197	$6_{10}-15$	0.1409	0.0002
MM	4.00	0	0.9998	0	0.9973	0	0.9953	0	0.9897	0	0.9976	0.9821
	2.00	0	0.9992	0	0.9999	0	1.0000	0	1.0000	0	1.0000	1.0000
$l=0$	1.00	0	0.9985	0	0.9999	0	0.9999	0	1.0000	0	0.9999	1.0000
	0.50	0	0.7653	0	0.8650	0	0.9842	0	0.9317	0	0.9881	0.9322
$k=0.5$	0.25	0	0.0289	0	0.3984	0	0.6752	0	0.8284	0	0.0223	0.0358
LS	4.00	$2_{10}-4$	0.9994	$5_{10}-5$	0.9905	$9_{10}-7$	0.9842	$4_{10}-9$	0.9819	$6_{10}-13$	0.9909	0.9941
	2.00	$3_{10}-4$	0.9995	$4_{10}-7$	0.9999	$1_{10}-10$	1.0000	$3_{10}-13$	1.0000	$9_{10}-18$	1.0000	1.0000
$l=0$	1.00	$9_{10}-5$	0.9998	$3_{10}-9$	1.0000	$9_{10}-11$	1.0000	$2_{10}-13$	1.0000	$4_{10}-16$	1.0000	1.0000
	0.50	$8_{10}-4$	0.9752	$2_{10}-5$	0.9782	$2_{10}-8$	0.9967	$4_{10}-12$	0.9990	$7_{10}-13$	0.9972	0.9993
$k=0.5$	0.25	$2_{10}-4$	0.2067	$2_{10}-4$	0.3855	$5_{10}-7$	0.6228	$7_{10}-9$	0.6514	$3_{10}-11$	0.0636	0.1566
MM	4.00	0	0.9946	0	0.9990	0	0.9979	0	0.9905	0	0.9997	0.9966
	2.00	0	0.9993	0	0.9999	0	0.9999	0	1.0000	0	0.9999	1.0000
$l=0$	1.00	0	0.9996	0	0.9999	0	0.9999	0	1.0000	0	0.9999	1.0000
	0.50	0	0.9936	0	0.9606	0	0.9796	0	0.9334	0	0.9910	0.9159
$k=1.0$	0.25	0	0.8685	0	0.0323	0	0.6849	0	0.8905	0	0.0086	0.0089
LS	4.00	$9_{10}-4$	0.9961	$2_{10}-6$	0.9967	$7_{10}-8$	0.9953	$7_{10}-11$	0.9608	$2_{10}-12$	0.9981	0.9798
	2.00	$1_{10}-4$	0.9999	$4_{10}-7$	0.9999	$6_{10}-10$	0.9999	$3_{10}-13$	1.0000	$7_{10}-17$	0.9999	1.0000
$l=0$	1.00	$6_{10}-5$	0.9989	$6_{10}-9$	0.9999	$3_{10}-10$	0.9999	$7_{10}-14$	1.0000	$1_{10}-16$	0.9999	1.0000
	0.50	$4_{10}-4$	0.9980	$2_{10}-5$	0.9959	$2_{10}-7$	0.9955	$4_{10}-10$	0.9974	$4_{10}-12$	0.9946	0.9979
$k=1.0$	0.25	$2_{10}-3$	0.8935	$8_{10}-6$	0.0075	$4_{10}-6$	0.6571	$2_{10}-8$	0.8752	$8_{10}-11$	0.1004	0.0064
MM	2.00	0	0.9155	0	0.9451	0	0.9720	0	0.9909	0	0.9052	0.9928
	1.00	0	0.8782	0	0.9638	0	0.9955	0	0.9999	0	0.9887	0.9970
$l=1$	0.50	0	0.8867	0	0.9669	0	0.9802	0	0.9636	0	0.9566	0.9925
	0.40	0	0.5878	0	0.2267	0	0.7170	0	0.0545	0	0.0465	0.5823
$k=0.2$	0.30	0	0.0001	0	0.4551	0	0.8402	0	0.9673	0	0.1436	0.0441
	0.20	0	0.0631	0	0.7936	0	0.9022	0	0.9743	0	0.0934	0.0061
LS	2.00	$5_{10}-2$	0.9182	$3_{10}-3$	0.9528	$2_{10}-4$	0.9722	$7_{10}-6$	0.9745	$3_{10}-7$	0.9448	0.9859
	1.00	$3_{10}-3$	0.9105	$2_{10}-5$	0.9790	$9_{10}-8$	0.9985	$2_{10}-11$	0.9999	$9_{10}-12$	0.9945	0.9975
$l=1$	0.50	$3_{10}-6$	0.9580	$2_{10}-7$	0.9970	$1_{10}-9$	0.9960	$1_{10}-12$	0.9976	$2_{10}-14$	0.9890	0.9999
	0.40	$2_{10}-5$	0.9492	$1_{10}-6$	0.8950	$4_{10}-9$	0.9645	$4_{10}-12$	0.9493	$1_{10}-13$	0.8151	0.9640
$k=0.2$	0.30	$4_{10}-5$	0.4082	$4_{10}-6$	0.3257	$7_{10}-10$	0.8541	$6_{10}-13$	0.8252	$4_{10}-15$	0.0095	0.1127
	0.20	$8_{10}-6$	0.0869	$2_{10}-7$	0.8239	$5_{10}-11$	0.8901	$1_{10}-14$	0.7777	$3_{10}-17$	0.0519	0.0134
MM	4.00	0	0.9326	0	0.9870	0	0.2346	0	0.2859	0	0.9818	0.0385
	2.00	0	0.9791	0	0.9987	0	0.9962	0	0.9999	0	0.9885	0.9974
$l=1$	1.00	0	0.9983	0	0.9964	0	0.9994	0	0.9998	0	0.9966	0.9993
	0.50	0	0.8242	0	0.9628	0	0.9751	0	0.9864	0	0.9726	0.9894
$k=0.5$	0.25	0	0.0213	0	0.5797	0	0.7315	0	0.9214	0	0.0054	0.0997

Table 1 (continued)

	γ	λ_1	S_{12}	λ_2	S_{23}	λ_3	S_{34}	λ_4	S_{45}	λ_5	S_{3e}	S_{5e}
LS	4.00	$4_{10}-2$	0.9456	$1_{10}-3$	0.9175	$2_{10}-4$	0.0191	$6_{10}-5$	0.0212	$2_{10}-6$	0.9208	0.0056
	2.00	$5_{10}-3$	0.9967	$6_{10}-5$	0.9941	$9_{10}-6$	0.9975	$3_{10}-9$	0.9947	$2_{10}-8$	0.9930	0.9938
$l=1$	1.00	$1_{10}-4$	0.9928	$3_{10}-6$	0.9993	$2_{10}-8$	0.9989	$9_{10}-11$	0.9999	$5_{10}-12$	0.9965	0.9994
	0.50	$7_{10}-4$	0.9364	$1_{10}-6$	0.9938	$6_{10}-9$	0.9952	$2_{10}-12$	0.9995	$1_{10}-13$	0.9933	0.9996
$k=0.5$	0.25	$1_{10}-4$	0.0062	$3_{10}-5$	0.5341	$6_{10}-8$	0.6588	$2_{10}-9$	0.7693	$9_{10}-12$	0.0029	0.1168
MM	4.00	0	0.9937	0	0.9961	0	0.8707	0	0.7068	0	0.9898	0.7544
	2.00	0	0.9921	0	0.9978	0	0.9996	0	0.9999	0	0.9950	0.9979
$l=1$	1.00	0	0.9758	0	0.9992	0	0.9997	0	0.9999	0	0.9963	0.9985
	0.50	0	0.8958	0	0.8346	0	0.7550	0	0.4972	0	0.9667	0.8197
$k=1.0$	0.25	0	0.0104	0	0.4527	0	0.3824	0	0.8916	0	0.0010	0.0000
LS	4.00	$7_{10}-4$	0.9850	$3_{10}-5$	0.9805	$4_{10}-6$	0.8285	$1_{10}-8$	0.0485	$2_{10}-8$	0.9754	0.1104
	2.00	$4_{10}-4$	0.9955	$9_{10}-6$	0.9975	$3_{10}-8$	0.9990	$6_{10}-10$	0.9995	$2_{10}-10$	0.9948	0.9983
$l=1$	1.00	$5_{10}-5$	0.9930	$3_{10}-6$	0.9976	$6_{10}-9$	0.9996	$4_{10}-11$	0.9998	$4_{10}-13$	0.9955	0.9988
	0.50	$4_{10}-4$	0.9860	$4_{10}-5$	0.9345	$1_{10}-8$	0.9245	$1_{10}-9$	0.9613	$1_{10}-11$	0.9657	0.9970
$k=1.0$	0.25	$1_{10}-3$	0.8545	$3_{10}-5$	0.0660	$1_{10}-6$	0.6699	$1_{10}-10$	0.8562	$5_{10}-12$	0.0000	0.0219
MM	2.00	0	0.7574	0	0.8543	0	0.9011	0	0.9588	0	0.4685	0.8457
	1.00	0	0.5938	0	0.6459	0	0.9034	0	0.9851	0	0.7920	0.9969
$l=2$	0.50	0	0.7565	0	0.1634	0	0.8788	0	0.9997	0	0.9066	0.9953
	0.40	0	0.7554	0	0.8032	0	0.1064	0	0.0735	0	0.7749	0.9695
$k=0.2$	0.30	0	0.8788	0	0.0039	0	0.9233	0	0.9304	0	0.5535	0.8208
	0.20	0	0.7239	0	0.0247	0	0.9645	0	0.8259	0	0.3134	0.1147
LS	2.00	$2_{10}-1$	0.7914	$6_{10}-3$	0.8684	$3_{10}-4$	0.8936	$2_{10}-5$	0.8451	$2_{10}-6$	0.5982	0.8700
	1.00	$3_{10}-2$	0.6094	$1_{10}-4$	0.8355	$4_{10}-7$	0.9509	$2_{10}-9$	0.9913	$8_{10}-12$	0.8995	0.9987
$l=2$	0.50	$7_{10}-4$	0.4259	$1_{10}-6$	0.3039	$9_{10}-11$	0.9963	$2_{10}-14$	0.9989	$4_{10}-15$	0.9970	0.9997
	0.40	$9_{10}-5$	0.0194	$6_{10}-8$	0.4271	$4_{10}-11$	0.9948	$3_{10}-13$	0.9607	$1_{10}-14$	0.9748	0.9998
$k=0.2$	0.30	$6_{10}-6$	0.6821	$2_{10}-8$	0.1459	$2_{10}-11$	0.8346	$2_{10}-14$	0.1695	$2_{10}-16$	0.4516	0.9918
	0.20	$3_{10}-7$	0.7042	$1_{10}-9$	0.5908	$4_{10}-13$	0.8853	$9_{10}-16$	0.7535	$2_{10}-17$	0.2648	0.2214
MM	4.00	0	0.5771	0	0.5726	0	0.1955	0	0.3956	0	0.6765	0.0112
	2.00	0	0.4730	0	0.9681	0	0.9930	0	0.9875	0	0.9262	0.9779
$l=2$	1.00	0	0.3591	0	0.9840	0	0.9992	0	0.9976	0	0.9772	0.9930
	0.50	0	0.8184	0	0.7657	0	0.9657	0	0.6470	0	0.9500	0.7591
$k=0.5$	0.25	0	0.1619	0	0.7381	0	0.7963	0	0.9058	0	0.0202	0.0028
LS	4.00	$3_{10}-1$	0.5386	$3_{10}-2$	0.2266	$1_{10}-3$	0.0095	$5_{10}-5$	0.0562	$2_{10}-4$	0.3601	0.0009
	2.00	$6_{10}-2$	0.7082	$5_{10}-4$	0.9961	$1_{10}-5$	0.9727	$9_{10}-7$	0.9855	$2_{10}-8$	0.9257	0.9855
$l=2$	1.00	$4_{10}-3$	0.9433	$2_{10}-6$	0.9803	$3_{10}-9$	0.9992	$5_{10}-10$	0.9970	$2_{10}-12$	0.9821	0.9960
	0.50	$3_{10}-5$	0.9916	$3_{10}-7$	0.9643	$9_{10}-10$	0.9856	$4_{10}-12$	0.9919	$3_{10}-13$	0.9747	0.9940
$k=0.5$	0.25	$8_{10}-5$	0.1509	$7_{10}-7$	0.7483	$3_{10}-9$	0.7406	$9_{10}-11$	0.9094	$5_{10}-12$	0.1254	0.0047
MM	4.00	0	0.9324	0	0.9226	0	0.8334	0	0.0394	0	0.9237	0.1926
	2.00	0	0.9630	0	0.9966	0	0.9955	0	0.9967	0	0.9502	0.9862
$l=2$	1.00	0	0.9934	0	0.9998	0	0.9940	0	0.9997	0	0.9614	0.9876
	0.50	0	0.0682	0	0.3223	0	0.0220	0	0.0749	0	0.6406	0.2214
$k=1.0$	0.25	0	0.5288	0	0.5360	0	0.9211	0	0.8699	0	0.0018	0.0116
LS	4.00	$9_{10}-3$	0.9648	$5_{10}-4$	0.8960	$9_{10}-7$	0.3780	$9_{10}-7$	0.0396	$2_{10}-8$	0.9150	0.0828
	2.00	$3_{10}-4$	0.9648	$1_{10}-6$	0.9897	$5_{10}-7$	0.9976	$2_{10}-8$	0.9975	$2_{10}-10$	0.9671	0.9870
$l=2$	1.00	$6_{10}-4$	0.9855	$9_{10}-8$	0.9974	$2_{10}-8$	0.9970	$4_{10}-11$	0.9994	$7_{10}-12$	0.9730	0.9920
	0.50	$5_{10}-3$	0.5578	$9_{10}-5$	0.5385	$6_{10}-8$	0.3390	$8_{10}-10$	0.4531	$1_{10}-11$	0.7176	0.8623
$k=1.0$	0.25	$1_{10}-3$	0.2483	$2_{10}-5$	0.8088	$2_{10}-6$	0.6371	$3_{10}-9$	0.7383	$6_{10}-10$	0.0019	0.0396

Table 1 (continued)

	γ	λ_1	S_{12}	λ_2	S_{23}	λ_3	S_{34}	λ_4	S_{45}	λ_5	S_{3e}	S_{5e}
MM	1.00	0	0.9030	0	0.8980	0	0.2998	0	0.6892	0	0.8101	0.8457
	0.50	0	0.8629	0	0.9766	0	0.1641	0	0.8297	0	0.7434	0.9467
$l=3$	0.40	0	0.9318	0	0.0236	0	0.2569	0	0.9901	0	0.0700	0.9667
	0.30	0	0.2113	0	0.1284	0	0.9353	0	0.9219	0	0.7497	0.9999
$k=0.2$	0.25	0	0.0190	0	0.5451	0	0.9635	0	0.0575	0	0.8326	0.5374
	0.20	0	0.4717	0	0.7612	0	0.9684	0	0.0298	0	0.0765	0.9178
LS	1.00	$8_{10}-2$	0.7800	$9_{10}-4$	0.0888	$4_{10}-6$	0.5609	$1_{10}-9$	0.9455	$9_{10}-10$	0.1956	0.9452
	0.50	$3_{10}-4$	0.8800	$2_{10}-8$	0.9249	$1_{10}-10$	0.2876	$1_{10}-10$	0.9295	$3_{10}-14$	0.6563	0.9790
$l=3$	0.40	$3_{10}-5$	0.9541	$2_{10}-10$	0.1091	$8_{10}-11$	0.6094	$3_{10}-14$	0.9940	$5_{10}-16$	0.4366	0.9848
	0.30	$1_{10}-6$	0.0021	$5_{10}-10$	0.2116	$2_{10}-13$	0.9957	$4_{10}-14$	0.9272	$5_{10}-16$	0.9196	0.9999
$k=0.2$	0.25	$5_{10}-8$	0.2456	$1_{10}-9$	0.9352	$9_{10}-13$	0.8917	$2_{10}-15$	0.9970	$1_{10}-15$	0.8786	0.9987
	0.20	$1_{10}-8$	0.9945	$5_{10}-10$	0.1613	$9_{10}-13$	0.9867	$3_{10}-16$	0.8976	$2_{10}-17$	0.9509	0.8195
MM	4.00	0	0.2764	0	0.3168	0	0.0006	0	0.6555	0	0.2625	0.0218
	2.00	0	0.0784	0	0.6387	0	0.9938	0	0.9829	0	0.8225	0.9167
$l=3$	1.00	0	0.2434	0	0.3485	0	0.8845	0	0.9860	0	0.7718	0.9391
	0.50	0	0.0863	0	0.3974	0	0.0008	0	0.5918	0	0.7628	0.0613
$k=0.5$	0.25	0	0.3279	0	0.1687	0	0.9871	0	0.8728	0	0.0347	0.0893
LS	4.00	$9_{10}-1$	0.2553	$7_{10}-2$	0.0424	$7_{10}-3$	0.0613	$3_{10}-4$	0.2315	$2_{10}-5$	0.1484	0.0224
	2.00	$3_{10}-1$	0.1148	$1_{10}-3$	0.8665	$4_{10}-6$	0.9943	$9_{10}-7$	0.9417	$3_{10}-7$	0.8642	0.9437
$l=3$	1.00	$4_{10}-4$	0.9665	$3_{10}-5$	0.9542	$3_{10}-7$	0.9631	$2_{10}-10$	0.9969	$4_{10}-10$	0.8894	0.9886
	0.50	$4_{10}-4$	0.5910	$7_{10}-7$	0.6253	$1_{10}-9$	0.1961	$9_{10}-11$	0.0545	$3_{10}-11$	0.9303	0.2387
$k=0.5$	0.25	$8_{10}-6$	0.1652	$9_{10}-8$	0.7793	$4_{10}-10$	0.0732	$1_{10}-11$	0.4113	$3_{10}-10$	0.0336	0.1120
MM	4.00	0	0.2557	0	0.9521	0	0.7771	0	0.5364	0	0.7020	0.2979
	2.00	0	0.9489	0	0.9268	0	0.9768	0	0.9971	0	0.8309	0.9404
$l=3$	1.00	0	0.4121	0	0.6843	0	0.9740	0	0.9912	0	0.8448	0.9688
	0.50	0	0.0979	0	0.1795	0	0.1812	0	0.7918	0	0.1643	0.0096
$k=1.0$	0.25	0	0.5027	0	0.0497	0	0.9124	0	0.9164	0	0.0065	0.0143
LS	4.00	$5_{10}-2$	0.6278	$2_{10}-4$	0.7757	$5_{10}-5$	0.6028	$1_{10}-6$	0.0002	$2_{10}-7$	0.6945	0.0960
	2.00	$2_{10}-4$	0.9235	$9_{10}-3$	0.9718	$1_{10}-6$	0.9874	$1_{10}-8$	0.9871	$1_{10}-9$	0.8485	0.9569
$l=3$	1.00	$4_{10}-4$	0.7855	$2_{10}-5$	0.9529	$9_{10}-8$	0.9816	$5_{10}-10$	0.9964	$1_{10}-10$	0.8706	0.9671
	0.50	$2_{10}-2$	0.0098	$4_{10}-5$	0.4937	$1_{10}-7$	0.1055	$4_{10}-9$	0.6085	$2_{10}-9$	0.5533	0.0456
$k=1.0$	0.25	$1_{10}-3$	0.4236	$5_{10}-6$	0.8435	$2_{10}-6$	0.6089	$3_{10}-9$	0.0832	$2_{10}-9$	0.0070	0.0158

As noted already, the quantities S_{ij} listed in Table 1 are fairly sensitive to the fine details of the approximate wave function. As, in addition, S_{ij} is not the quantity that we directly optimize, it is not necessarily monotoneously improved when the number of variational parameters is increased. Examples of this can be seen in Table 1, mainly at γ values lying very far from the optimum. Naturally the stability test indicates in these cases the inaccuracy of the result.

In Table 2 the averages of the $S_{i,i+1}$-values are given as a function of γ for $l=1$ and $k=0.2$, 0.5, 1.0. In Table 3 phase shifts calculated for $l=0$ presented.

For comparison also the exact phase shift values calculated from scattering amplitude values published by Morawitz [5] are included in Table 3.

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Table 2. *Averages of the values* $S_{i,i+1}$. $\bar{S} = \frac{1}{4}\sum_{i=1}^{4} S_{i,i+1}$ *for* $l=1$

	γ	$k=0.2$	$k=0.5$	$k=1.0$
MM	4.00	0.5437	0.6100	0.8918
	3.50	0.5683	0.6582	0.8914
	2.50	0.9353	0.9861	0.9967
	2.00	0.9559	0.9935	0.9973
	1.50	0.9564	0.9969	0.9977
	1.00	0.9593	0.9989	0.9936
	0.75	0.9669	0.9951	0.9898
	0.50	0.9743	0.9371	0.7456
	0.25	0.6314	0.5635	0.4345
LS	4.00	0.3024	0.4758	0.7106
	3.50	0.3867	0.5141	0.8902
	2.50	0.7621	0.9664	0.9951
	2.00	0.9544	0.9957	0.9978
	1.50	0.9659	0.9981	0.9987
	1.00	0.9719	0.9977	0.9975
	0.75	0.9786	0.9953	0.9938
	0.50	0.9871	0.9812	0.9516
	0.25	0.5988	0.4921	0.6116

Table 3. *Phase shifts for* $l=0$ *and* $\gamma=1.5$

	k	Approximation					Exact.
		1	2	3	4	5	(Morawitz [5])
MM	0.1	−0.979045	−0.980476	−0.979939	−0.979876	−0.979873	−0.979879
	0.5	2.445098	2.638331	2.638680	2.638778	2.638771	2.638776
	0.9	1.069617	1.108165	1.112643	1.113387	1.113431	1.113454
LS	0.1	−0.980254	−0.980256	−0.979905	−0.979875	−0.979873	−0.979879
	0.5	2.534985	2.636095	2.638749	2.638760	2.638768	2.638776
	0.9	1.088185	1.110106	1.113012	1.113404	1.113448	1.113454

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