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Bound states in dipole fields and continuity properties of electronic spectra

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Abstract. We discuss some known binding/no-binding criteria for a charged particle moving in the field of a neutral system of N fixed point charges. As an application, we derive a uniform Lipschitz property (with respect to nuclear configurations) of the discrete spectrum of electronic Hamiltonians.

1. Introduction

This note was inspired by a recent review article [1] on the 'minimum dipole moment required to bind an electron', where the history of the subject is traced back to Fermi's notebooks. Our remarks (i)–(iv) below are intended to summarize, to simplify and to correct some of the original arguments (see [1] for a more extensive bibliography).

(i) The critical dipole moment a_0 is defined as the maximum value of $a = |\mathbf{a}|$ such that

$$H_0 = -\Delta + r^{-3}(\mathbf{a}, \mathbf{x}) \geqslant 0, \tag{1}$$

where $r = |\mathbf{x}|$. As a result of numerical work (see e.g. [2]),

$a_0 = 1.278630.$

The qualitative aspects of this problem are briefly reviewed in Section 2, where we also derive simple upper and lower bounds for a_0 with an accuracy of the order of 1%.

(ii) A variational argument of Simon [3] shows that the field of any neutral system of N fixed point charges produces infinitely many bound states if its dipole moment a exceeds a_0 (Section 3).

(iii) It is incorrect [1, 2, 4] that the converse (no binding for $a \leqslant a_0$) follows from the scaling property (10) of the eigenvalue problem: (10) holds for arbitrary N, but for $N \geqslant 3$ there is no 'minimum dipole moment required to bind an electron' (section 4).

(iv) That no binding occurs for $N = 2$ and $a \leqslant a_0$ can be seen from a different law of corresponding states, particular to 2-point dipoles and simply expressed in terms of elliptic coordinates. From this one can derive (sufficient) no-binding conditions for $N \geqslant 3$ (Section 5).

In the last part of this paper we consider the Hamiltonian $H(y)$ of n electrons moving in the field of N arbitrary point charges fixed in the configuration $y=(y_1 \cdots y_N) \in R^{3N}$. Using the no-binding theorem for 2-point dipoles we derive a uniform Lipschitz property of the discrete spectrum of $H(y)$ as a function of y.

2. The particle in a pure dipole field

The Hamiltonian (1) can be written as

$$H_0 = -\frac{1}{r}\frac{\partial^2}{\partial r^2} r + r^{-2}\Lambda,$$

$$\Lambda = L^2 + r^{-1}(\mathbf{a}, \mathbf{x}),$$

where L^2 is the square of the angular momentum. Since $(\mathbf{a}, \mathbf{x})/r$ is bounded, Λ is a self-adjoint operator on $L^2(\Omega)$ (Ω = unit sphere). In the subspaces $\mathscr{H}_{\pm m}$ ($m = 0, 1, 2, \ldots$) of states with angular momentum $\pm m$ along the axis $\mathbf{a}$ it acts as the operator

$$\Lambda_m(a) = -\frac{d}{dz}(1-z^2)\frac{d}{dz} + m^2(1-z^2)^{-1} + az$$

on $L^2(-1, +1)$, where $z = (\mathbf{a}, \mathbf{x})/ar$. Λ_m has a complete orthonormal system of eigenfunctions

$$\Lambda_m f_{ml} = \lambda_{ml} f_{ml} \quad (l = m, m+1, \ldots), \tag{2}$$

where $\lambda_{ml}(a)$ is the eigenvalue converging to $l(l+1)$ as $a \to 0$. Since in this process the eigenvalues cannot cross, l always labels the $\lambda_{ml}(a)$ in ascending order. It follows from the operator inequalities

$$\Lambda_m(a) \geqslant \Lambda_n(a) \quad (\text{for } m \geqslant n)$$

and

$$\Lambda_m(a) \geqslant \Lambda_m(0) - a$$

that $\lambda_{m,m+k}(a)$ increases with m for fixed k and that

$$\lambda_{ml}(a) \geqslant l(l+1) - a. \tag{3}$$

In particular, λ_{00} is always the lowest eigenvalue of Λ and the only candidate for a negative eigenvalue as long as $a \leqslant 2$. In order to find simple estimates for $\lambda_{00}(a)$ we transform $(f, \Lambda_0 f)$ by partial integration into

$$(f, \Lambda_0 f) = \int_{-1}^{+1} dz (1-z^2)\left(\left|f' + \frac{a}{2} f\right|^2 - \frac{a^2}{4}|f|^2\right),$$

where $f' = df/dz$. This gives the lower bound

$$\lambda_{00}(a) \geqslant -a^2/4, \tag{4}$$

improving (3) for $a < 4$, and it suggests the choice $f \sim \exp(-az/2)$ (i.e.

$f' + af/2 = 0$) to obtain the upper bound

$$\lambda_{00}(a) \leqslant (f, \Lambda_0 f) = \tfrac{1}{2}(1 - a/\mathrm{Th}\, a). \tag{5}$$

Hence $\lambda_{00}(a)$ is indeed negative for $a > 0$ and strictly decreasing to $-\infty$ as $a \to +\infty$, since

$$\lambda'_{00}(a) = (f_{00}, z f_{00}) < \lambda_{00}(a)/a.$$

Let (r, θ, ϕ) be polar coordinates with respect to the axis a. The subspaces $\mathscr{H}_{\pm m,l}$ of the states

$$r^{-1} u(r) f_{ml}(\cos\theta) e^{\pm im\phi} \quad (u \in L^2(0, \infty))$$

are invariant under H_0, which acts on u as the operator

$$h(\lambda_{ml}) = -\frac{d^2}{dr^2} + \lambda_{ml} r^{-2}$$

on $L^2(0, \infty)$. We shall use this operator only on the domain $C_0^\infty(0, \infty)$ of infinitely differentiable functions $u(r)$ vanishing outside some finite, strictly positive interval. (To define the *dynamics* of a particle in a pure dipole field we should choose, in each $\mathscr{H}_{\pm ml}$, a selfadjoint or possibly non-selfadjoint [5] extension of $h(\lambda_{ml})$. This is not necessary in the present context.) It is well known (see e.g. [3]) that $h(\lambda) \geqslant 0$ if and only if $\lambda \leqslant -1/4$, i.e.

$$\sup_{0 \neq u \in C_0^\infty(0,\infty)} (u, r^{-2} u)(u', u')^{-1} = 4, \tag{6}$$

where $u' = du/dr$. Consequently, $H_0 \geqslant 0$ on $C_0^\infty(R^3 \backslash \{0\})$ if and only if $\lambda_{00}(a) \geqslant -\frac{1}{4}$. This is equivalent to $a \leqslant a_0$, where a_0 is uniquely defined by $\lambda_{00}(a_0) = -\frac{1}{4}$. The upper bound

$$a_0 < 1.288$$

is obtained from (5) as the positive solution of $\mathrm{Th}\, a = 2a/3$. (4) gives the lower bound $a_0 > 1$. This can be improved using Temple's inequality [6]:

$$\lambda_{00} \geqslant (f, \Lambda_0 f) - [(f, \Lambda_0^2 f) - (f, \Lambda_0 f)^2][\lambda_{01} - (f, \Lambda_0 f)]^{-1}$$

with $f(z) \sim \exp(-az/2)$ and with the estimate (3) for λ_{01}. The resulting lower bound

$$a_0 > 1.245$$

is the positive solution of $\mathrm{Th}\, a = (4a^2 + 5a)(4a^2 + 6a + 1)^{-1}$.

3. Binding in dipole fields

Let $e = (e_1 \cdots e_N)$, $\sum e_i = 0$, be N point charges in a fixed configuration $y = (\mathbf{y}_1 \cdots \mathbf{y}_N)$, and $\mathbf{a} = \sum e_i \mathbf{y}_i$ their dipole moment. It follows from a result of Simon [3] that

$$H(e, y) = -\Delta + \sum_{i=1}^{N} e_i |\mathbf{x} - \mathbf{y}_i|^{-1} = -\Delta + V(\mathbf{x}) \tag{7}$$

has infinitely many bound states if $a > a_0$. We restate Simon's estimate in a form which directly applies to this case.

Lemma 1 (Simon). *Assume that for some $R > 0$, $V(\mathbf{x})$ is a real, locally integrable function for $R < |\mathbf{x}| < \infty$ satisfying*

$$V(\mathbf{x}) - (\mathbf{a}, \mathbf{x}) r^{-3} \leq c r^{-p},$$

with c arbitrary and $2 < p$. If $a > a_0$, there exists an infinite sequence of C^∞-functions ψ_n with compact, disjoint supports in $R < |\mathbf{x}| < \infty$ such that

$$(\Psi_n, (-\Delta + V)\Psi_n) < 0.$$

Remark. Since $H(e, y)$ is selfadjoint on the domain of the Laplacian and has essential spectrum $[0, \infty)$, Simon's lemma proves the existence of an infinite sequence of negative eigenvalues of $H(e, y)$ converging to zero if $a > a_0$ [6].

Proof. Let $\psi = r^{-1} u(r) f_{00}(\cos\theta)$, with f_{00} given by (2), and $h = h(\lambda)$, $\lambda = \lambda_{00}(a) < -\frac{1}{4}$. According to (6) we can find $u \in C_0^\infty(0,\infty)$ such that $(u, u) = 1$ and $(u, hu) < 0$. The unitary scaling operator

$$U(s) : \psi(\mathbf{x}) \to \psi_s(\mathbf{x}) \equiv s^{3/2} \psi(s\mathbf{x}) \tag{8}$$

$(0 < s < \infty)$ acts on the radial wave function u as

$$u(r) \to u_s(r) \equiv s^{1/2} u(sr).$$

For s sufficiently small we have $u_s \in C_0^\infty(R, \infty)$ and also

$$\begin{aligned}(\psi_s, (-\Delta + V)\psi_s) &\leq (u_s, hu_s) + c(u_s, r^{-p} u_s) \\ &= s^2 (u, hu) + c s^p (u, r^{-p} u) \\ &< 0.\end{aligned}$$

Since u has compact support not containing 0, we can choose a sequence $s = s(n) \to 0$ $(n = 1, 2, \ldots)$ such that the scaled functions $u_{s(n)}$ have pairwise disjoint supports.

4. The scaling argument

$H(e, y)$ has the scaling property

$$U(s) H(e, y) U^{-1}(s) = s^2 H(s^{-1} e, sy) \tag{9}$$

with respect to the transformation (8). Hence $H(e, y)\psi = E\psi$ is equivalent to

$$H(s^{-1} e, sy)\psi_s = s^{-2} E \psi_s \tag{10}$$

Since the scaling $(e, y) \to (s^{-1} e, sy)$ does not affect the dipole moment, the scaled potential converges (for $\mathbf{x} \neq 0$) to the pure dipole potential as $s \to 0$. On the basis of (10) it has been argued [1, 2, 4] that the 2-point dipole $(N = 2)$ has no bound states if $a < a_0$. For example: If $E < 0$, then $s^{-2} E \to -\infty$ as $s \to 0$. Conclusion: $a > a_0$, since the resulting pure dipole will have states of 'infinitely large negative energy'.

While this conclusion is correct for $N = 2$, the argument must be false since it

applies equally well to arbitrary N. But for $N \geq 3$ there are obvious counterexamples with $a = 0$ where binding occurs: place two charges $+1$ a distance R apart and a third charge -2 at middistance. For large R there will be slightly perturbed hydrogen-like bound states around the negative charge.

The scaling argument fails since the scaled eigenfunctions ψ_s do not converge to a corresponding state in the pure dipole field ($\psi_s \to 0$ weakly as $s \to 0$). For *fixed* $\psi \in C_0^\infty(R^3 \setminus \{0\}$ it is true that

$$\lim_{s \to 0} (\psi, H(s^{-1}e, sy)\psi) = (\psi, H_0\psi).$$

Hence if $H(e, y) \geq 0$, then $H(s^{-1}e, sy) \geq 0$ by (9) and it follows that $H_0 \geq 0$. Thus the scaling argument proves binding for $a > a_0$ (as we have already seen in Section 3), but it fails to prove the converse.

5. No-binding criteria

A simple example is $H = H_0 + V(\mathbf{x})$, where H_0 is given by (1). Suppose that (roughly speaking) V is nonnegative and sufficiently repulsive to make H bounded below and that $V(\mathbf{x}) \to 0$ faster than $|x|^{-2}$ as $\mathbf{x} \to \infty$. Then it follows from the results of Sections 1 and 2 that H has no negative energy bound states if $a \leq a_0$ and infinitely many if $a > a_0$ [2].

It is remarkable that exactly the same distinction holds for the 2-point dipole:

Theorem 1 (Fermi, Teller [7]). *For $N = 2$ the Hamiltonian (7) has no negative energy bound states if $a \leq a_0$ and infinitely many if $a > a_0$.*

Proof. In [7] this result (together with the value $a_0 = 1.278$) is mentioned without proof. A proof (based on counting the number of nodes of the explicit zero-energy solution in elliptic coordinates) was indicated by Wightman [8] and presented in more detail by Crawford [9].

Since binding for $a > a_0$ follows from Lemma 1 we need only show that $H(e, y) \geq 0$ if $N = 2$ and $a \leq a_0$. This is seen by inspection from the expression of $(\psi, H(e, y)\psi)$ in elliptic coordinates:

Let $r_i = |x - y_i|$ $(i = 1, 2)$, $2R = |y_1 - y_2|$ and $a = 2Re_2$. Then the coordinates

$r = \frac{1}{2}(r_1 + r_2) - R$,

$z = (r_1 - r_2)/2R$,

ϕ = angle around the dipole axis,

have the range

$$K: 0 \leq r < \infty; \qquad -1 \leq z \leq +1; \ \phi \in \text{unit circle};$$

which is *independent* of R, and

$$(\psi, H(e, y)\psi) = \int_K dr\, dz\, d\phi \left\{ (r^2 + 2Rr) \left| \frac{\partial \psi}{\partial r} \right|^2 + (1 - z^2) \left| \frac{\partial \psi}{\partial z} \right|^2 + [(1 - z^2)^{-1} + R^2(r^2 + 2Rr)^{-1}] \left| \frac{\partial \psi}{\partial \phi} \right|^2 + az\, |\psi|^2 \right\}.$$

For fixed a and $R=0$ this reduces to the expression of $(\psi, H_0\psi)$ in polar coordinates ($z=\cos\theta$). If this is nonnegative for all $\psi \in C_0^\infty(K)$, the same is evidently true for $R>0$.

Remarks. (i) Comparing this proof with the scaling argument (Section 4) we note the following difference: while the *Hamiltonian* is scaled in the same way, the transformation of *states* is now defined by changing R and keeping $\psi(r, z, \phi)$ fixed. As a function of $\mathbf{x}$, ψ then changes with R and has a well-defined limit as $R \to 0$. In distinction to (10), this 'elliptic law of corresponding states' is not unitary and does not map eigenfunctions into eigenfunctions.

(ii) Any Hamiltonian of the type (7) can be written in the form

$$H(e, y) = -\Delta + \sum_k V_k(\mathbf{x}) \tag{11}$$

where each $V_k(\mathbf{x})$ is a 2-point dipole potential (Example: split $e=(1,-2,1)$ into $(1,-1,0)+(0,-1,1)$). Let a_k be the absolute value of the dipole moment of V_k and $a=\sum a_k$. Then

$$H(e, y) = \sum_k a^{-1} a_k (-\Delta + a a_k^{-1} V_k) \geqslant 0 \tag{12}$$

if $a \leqslant a_0$, since each term in this sum corresponds to a 2-point dipole with dipole moment a. Therefore no binding occurs if the sum of the *absolute values* of the 2-point dipole moments does not exceed a_0.

6. Application to electronic spectra

Let

$$V_y(x) = \sum_{i=1}^{N} e_i \, |x - y_i|^{-1}$$

be the potential produced by N *arbitrary* point charges $e_1 \cdots e_N$ ('nuclei') with the configuration $y=(y_1 \cdots y_N)$, and

$$H(y) = \sum_{k=1}^{n} [-\Delta_k + V_y(\mathbf{x}_k)] + \sum_{i<k}^{1 \cdots n} |x_i - x_k|^{-1}$$

the Hamiltonian of n 'electrons' moving in this field. The y-dependence of the discrete spectrum of $H(y)$ (if any) is basic for the theory of molecules. Continuity in y is the only general local property known so far [10] (Differentiability has been proved in important special cases: for $N=2$[10] and for nondegenerate eigenvalues in the case of arbitrary N[11]). The link between this problem and our subject is provided by the remark that $V_y - V_z$ is a sum of N 2-point dipole potentials with dipole moments $a_i = |e_i(y_i - z_i)|$. It follows from (11) (12) that

$$H(y) - H(z) \geqslant -\|y - z\| \, H_0 \tag{13}$$

where $H_0 = -\sum_{k=1}^{n} \Delta_k$ is the kinetic energy of the electrons and $\| \, \|$ a norm in the

configuration space of the nuclei defined by

$$\|y\| = a_0^{-1} \sum_{i=1}^{N} |e_i y_i|.$$

From (13) we can derive estimates for the spectrum of $H(y)$ using the minimax principle in the following form [12]: For $m = 1, 2, 3 \cdots$ let

$$E_m(y) = \inf_{\dim M = m} \sup_{\psi \in M, \|\psi\| = 1} (\psi, H(y)\psi), \tag{14}$$

where M ranges over the finite-dimensional subspaces of $D(H(y))$. Then

$$\lim_{m \to \infty} E_m(y) = \Sigma(y) \tag{15}$$

is the minimum value in the essential spectrum of $H(y)$ and the subsequence $\{E_m(y) < \Sigma(y)\}$ is the sequence of eigenvalues of $H(y)$ below $\Sigma(y)$ in ascending order.

Theorem. *There exists a constant β independent of m, y, z such that*

$$|E_m(y) - E_m(z)| \leq \beta \|y - z\| \tag{16}$$

and

$$\left|\Sigma(y) - \Sigma(z)\right| \leq \beta \|y - z\| \tag{17}$$

for all m, y, z.

Proof. We first recall some properties of $H(y)$ [6]: $H(y)$ is self-adjoint with domain $D(H_0)$ and has essential spectrum $[\Sigma(y), \infty)$ with $\Sigma(y) \leq 0$. There exist constants $\alpha, \beta > 0$ independent of y such that

$$(\psi, H_0\psi) \leq \alpha(\psi, H(y)\psi) + \beta(\psi, \psi) \tag{18}$$

for all y and all $\psi \in D(H_0)$.

Secondly, we remark that for fixed y the trial subspaces M in (14) may be restricted by the condition that

$$(\psi, H(y)\psi) \leq \left(\Sigma(y) + \varepsilon\right)(\psi, \psi) \leq \varepsilon(\psi, \psi)$$

for all $\psi \in M$, with arbitrarily small $\varepsilon > 0$. By (18), a weaker and y-independent restriction is

$$(\psi, H_0\psi) \leq (\alpha\varepsilon + \beta)(\psi, \psi).$$

Imposing this it follows from (13) (14) that

$$E_m(y) - E_m(z) \geq -(\alpha\varepsilon + \beta)\|y - z\|.$$

Letting $\varepsilon \to 0$ and interchanging y with z we obtain (16), from which (17) follows in the limit $m \to \beta$.

Remarks. (i) Let G be any euclidean transformation of R^3 and $Gy \equiv (G\mathbf{y}_1 \cdots G\mathbf{y}_N)$. Since $H(Gy)$ is unitarily equivalent to $H(y)$ we can replace $\|y - z\|$ in (16) and (17) by $\min_G \|Gy - z\|$.

(ii) Theorem 2 also holds for the restriction of $H(y)$ to any symmetry sector with respect to permutations of electrons, since (13) is invariant under permutations.

(iii) We expect, of course, that the discrete eigenvalues of $H(y)$ can be represented by smooth functions of y. But even in this case the increasingly ordered eigenvalues will only be Lipschitz in points y where smooth eigenvalues cross.

(iv) The Lipschitz constant β appearing in Theorem 2 is defined by (18) and can be estimated in terms of the parameters n, N, $e_1 \cdots e_N$. It gives an upper bound for the electronic contribution to the binding forces in a molecule and thus a lower bound for the internuclear distances (in the clamped nuclei approximation).

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